Cationic starches on cellulose surfaces

a study of polyelectrolyte adsorption

"The first man I saw was of a meagre aspect, with sooty hands and face, his hair and beard long, ragged and singed in several places. His clothes, shirt, and skin were all of the same colour. He had been eight years upon a project for extracting sunbeams out of cucumbers, which were to be put into vials hermetically sealed, and let out to warm the air in raw inclement summers. He told me, he did not doubt in eight years more, that he should be able to supply the Governor's gardens with sunshine at a reasonable rate; but he complained that his stock was low, and entreated me to give him something as an encouragement to ingenuity, especially since this had been a very dear season for cucumbers. I made him a small present, for my Lord had furnished me with money on purpose, because he knew their practise of begging from all who go to see them."

Jonathan Swift: Gulliver's Travels, Part 3, A Voyage to Laputa (1726)

Promotor: Dr. B.H. Bijsterbosch
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H.G.M. van de Steeg

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Proefschrift
ter verkrijging van de graad van doctor
in de landbouw- en milieuwetenschappen
op gezag van de rector magnificus,
dr. H.C. van der Plas,
in het openbaar te verdedigen
op dinsdag 14 april 1992
des namiddags te vier uur in de Aula
van de Landbouwuniversiteit te Wageningen.

CONTENTS

STELLINGEN

I

Daar vrijwel alle belangrijke trends in polyelectrolytadsorptie reeds in 1977 door Hesselink zijn beschreven, is de onderschatting van zijn werk door latere onderzoekers op dit terrein volstrekt onterecht.

F.Th. Hesselink: "On the theory of polyelectrolyte adsorption. The effect on adsorption behavior of the electrostatic contribution to the adsorption free energy", *Journal of Colloid and Interface Science*, **60**: 448 (1977).
Dit proefschrift, hoofdstuk 2.

II

In verband met de invloed van de zoutconcentratie kunnen in polyelectrolytadsorptie twee regimes onderscheiden worden, namelijk het "screening reduced adsorption" regime en het "screening enhanced adsorption" regime. Als de zoutconcentratie groter wordt, neemt in het eerste regime de adsorptie af, terwijl in het tweede de adsorptie dan juist stijgt.

Dit proefschrift, hoofdstuk 2.

III

Specifieke adsorptie van segmenten kan niet altijd desorptie van een polyelectrolyt door zout verhinderen.

Dit proefschrift, hoofdstukken 2 en 4.

IV

Het zou voor papiermakers geen verrassing moeten zijn dat "anionic trash" uit Ca^{2+}-ionen kan bestaan.

Dit proefschrift, hoofdstuk 5.

V

Voor het slagen van Innovatieve Onderzoeksprogramma's is het noodzakelijk dat de belanghebbende bedrijven actief meedenken met de onderzoek(st)ers.

VI

Door preoccupatie met hun eigen werk lopen experimentalisten die zelf een theorie ontwikkelen het risico dat zij belangrijke implicaties hiervan over het hoofd zien.

VII

Het grensvlak tussen kolloïdchemie en NMR is nog vrijwel onverkend.

VIII

Het milieubeleid van de Europese Gemeenschap is vaak weinig vooruitstrevend. Dit heeft onder meer te maken met de ongrijpbaarheid van de *baten* van milieumaatregelen. Deze leidt er namelijk toe dat concessies aan dwarsliggende lidstaten doorgaans bestaan uit vermindering van *kosten*.

F.W. Scharpf: "Die Politikverflechtungs-Falle: Europäische Integration und deutscher Föderalismus im Vergleich", *Politische Vierteljahresschrift* **26**(4):323-356 (1985).
J.D. Liefferink: "Probleme der Gestaltung einer gemeinschaftlichen Umweltpolitik - Der Fall der Luftverschmutzung durch Grossfeuerungsanlagen", te verschijnen in 1992.

IX

In het promotiereglement van de Landbouwuniversiteit worden vrouwen alleen expliciet genoemd in de opmerking "voor dames: de meisjesnaam", terwijl de promovendus uitsluitend wordt aangeduid met "hij". Dit valt moeilijk te rijmen met het streven van dezelfde instelling naar een groter aantal vrouwelijke promovendi.

X

Het is opmerkelijk dat in het Christendom de maagdelijkheid van Maria heeft geleid tot prediking van een ascetische levenshouding en onderdrukking van vrouwen, terwijl maagdelijkheid in de Griekse en Romeinse cultuur juist op vrijheid en onafhankelijkheid van de betreffende vrouw duidde.

Marina Warner: "Alone of all her sex. The myth and the cult of the virgin Mary", Picador, Londen (1976).

XI

Hoewel natuurwetenschappers denken dat zij op de hoogte moeten zijn van de relativiteitstheorie, is kennis van de geschiedenis der natuurwetenschappen veel nuttiger om hun activiteiten te relativeren.

XII

De originaliteit van een proefschrift zou beter uitkomen als voor het omslag een één-(of meer-)procentsregeling voor de kunsten werd toegepast.

H.G.M. van de Steeg
Cationic starches on cellulose surfaces, a study of polyelectrolyte adsorption
Wageningen, 14 april 1992

The work reported in this thesis ("Cationic starches on cellulose surfaces: a study of polyelectrolyte adsorption") was supported by the Dutch Program for Innovation Oriented Carbohydrate Research (IOP-k), with financial aid from the ministry of economic affairs and the ministry of agriculture, nature management and fisheries.

Cover design and photography: Daniël Loos, Wageningen.

1 INTRODUCTION

1.1 Starch and papermaking

Plant fibers are the basic material of which paper is made. These cellulosic fibers are the main constituents of plant cell walls and, for papermaking, they are mainly obtained from wood in a chemical (pulping) process.

A scheme of the papermaking process is given in figure 1. The first step is to disperse the fibers in water, usually a few grams per liter, after which they are beaten in the refiner to roughen the surface of the fibers, so that they will better stick together and therefore increase the dry strength of the paper. From the headbox the cellulose dispersion flows out on a moving, endless, fine mesh screen called the *wire*. Part of the water seeps through the holes in the screen and the fiber mat, which still contains about 80% of water, is formed. This part of the paper machine is often referred to as the *wet-end*. After formation, the fiber mat is pressed

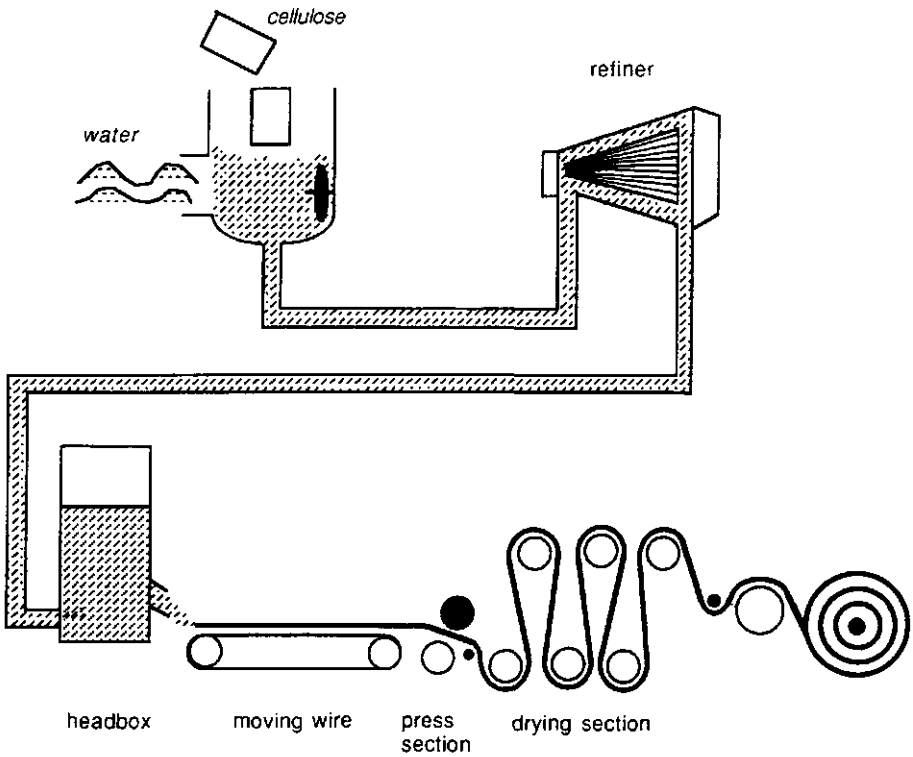

Figure 1. Schematic representation of the papermaking process

and dried, so that finally paper is obtained with a water content of 5-8%.

Apart from fibers, many other components are usually present in paper, namely the fillers (inorganic particles such as titaniumdioxide, clay or calciumcarbonate) and several chemicals of which starch is an important one. Starch constitutes the major food reserve of all the higher plants and is laid down in seeds, roots and tubers in the form of particles which are insoluble in cold water, the so-called starch granules. This means that starch must be cooked in order to be used in papermaking.

Starch is applied to improve the dry strength of paper and 0.5-2% on fiber dry weight is added somewhere between the refiner and the headbox (wet-end). If native starches are used for this purpose, the amount held in the sheet is rather low and papermakers say that the *retention* of starch is poor. According to Cushing and Schuman [1] the retention of native starches is about 60%, so that the rest is lost in process water (so-called *white water*). In the 1950's, researchers in applied starch chemistry tried to overcome this problem by synthesizing new starch derivatives. Cationic starch proved to be very effective, since at the generally encountered level of addition in paper industry, virtually 100% can be retained by fibers [2]. The first patent for a cationic starch for commercial use was issued in 1957 to Caldwell and Wurzburg [3].

Cationic starch improves dry strength by making the interfiber bonding stronger [4]. Beating requires energy and to save a portion of this expense, starch should be added to obtain a similar increase in strength. Addition of cationic starch is most effective if the starch paste is thoroughly cooked, so that most granules will be broken and thus the starch well dispersed [5]. Roberts et al [6] concluded that native starch and cationic starch equally improved paper strength if the retention was the same, and this is the reason that in most cases cationic starch is more effective.

In filled papers, for instance printing papers, the addition of cationic starch is of special importance. Fillers are highly desirable in printing papers, since they increase opacity and improve printing properties. Higher filler loads tend to improve the optical and printing properties, whereas economic considerations also seem to favour an increased use of fillers. However, the strength properties are severely impaired. Fortunately this loss in strength can be overcome by the addition of cationic starch [7, 8, 9]. Lindström and Florén [7] found that adding cationic starch in combination with an anionic polyacrylamide (a-PAM), is a very effective way of obtaining a sufficiently large amount of starch in their papers. They suggested that the cationic starch which was not

adsorbed onto the fibers and fillers, was precipitated onto these components in the form of a polyelectrolyte complex with a-PAM.

Cationic starch not only affects the dry strength, but also the retention of fines, small fiber parts, and fillers. Fines and fillers are much smaller than fibers and this means that it is difficult keeping them in the paper sheet (or in papermaking terms, to *retain* them) simply by the sieve working of the fiber web. Moreover, fibers, fines and fillers are all negatively charged and therefore repel each other. Large cationic polymers, like cationic starch, adsorb on these negatively charged surfaces and are able to flocculate fillers and fines with fibers by the formation of bridges. A good retention of fines and fillers also improves drainage of the wet web. It appears that the optimal amount of cationic starch as a retention aid, is much lower than the amount needed to obtain optimal dry strength [10]. So it is often considered more effective to use cationic starch as a dry strength agent in combination with another retention aid [11]. However, Alince et al. [9] have shown that in clay filled papers, added cationic starch both improves filler retention and increases strength, which makes the use of cationic starch superior to the use of only a synthetic retention aid (polyethylenimine).

The beneficial effects of cationic starch on papermaking and final paper quality, combined with its low price as compared to that of synthetic polymers, makes starch an important and popular wet-end additive, especially for fine papers. Apart from addition at the wet-end to improve the strength of paper, starch can also be added at the *size press*, located behind the drying section (figure 1). Starch solutions with concentrations between 5 and 15% are pressed into the rather dry paper sheet, so that it is absorbed quickly, and then the paper is dried again after the size press. Large volumes of starch are used at the size press, for instance in the production of board. The combination of wet-end and size press applications makes the paper industry the worlds largest purchaser of starch. Basic starches, used for cationics, are mostly from corn or potato. World wide corn starch remains dominant, while potato starch is a close second [12]. Although papermakers agree on the superiority of potato starch for wet-end applications [13], they buy more corn starch because it is cheaper. The lower price of corn starch also makes it the most popular starch for size press applications.

A good retention of cationic starch at the wet-end is very important. Loss of cationic starch not only means loss of dry strength, but also loss of fillers and fines and on top of that the process water and, eventually, the waste water, is polluted. Due to environmental legislation concerning the discharge of waste water, paper mills want their waste water to be as

clean as possible. Nowadays most paper mills operate with closed water circuits in order to use this water more effectively, so that polluted process water is a problem first inside and finally also outside the mill. Closure of the water circuits leads to higher concentrations of all kinds of substances in the process water [14, 15] and also the retention of cationic starch can become very poor. It is shown that substances such as aluminium sulphate (so-called *papermaker's alum*), which is often used, and anionic polymers dissolving from wood [16], reduce the retention of cationic starch.

1.2 A colloid-chemical approach

Although cationic starch is used to such a large extent, neither the mechanism by which it is retained by cellulose fibers, nor the way in which the retention is disturbed, are well understood. Only a small amount of the research efforts in the field of papermaking is devoted to starch. The reason for this could be twofold. Firstly, starch is such a common chemical that it is not considered worthy of research. This was once expressed to the author in the following way: "Starch? You just dig it out of the ground!" Secondly, for those interested in the retention mechanism, the combination of starch and cellulose fibers is far too complex, since neither the characteristics of starch nor those of cellulose fibers are thoroughly known. As stated by Wågberg and Ödberg [17]: "The porous nature of the fibers obviously makes it important to use well characterized polymers for adsorption studies".

In line with the last anotation, this study was undertaken as a first step to gain more fundamental knowledge about the retention, or in colloid-chemical terms, the adsorption of cationic starch on cellulose and how it can be disturbed. Our approach is a colloid-chemical one, which means that our experimental system was kept as simple as possible in order to facilitate physical interpretation and was therefore far from the reality of papermaking. This has been done very seldom, especially in research related to starch. We studied the adsorption of two different kinds of cationic starch on microcrystalline cellulose as a model for cellulose fibers, in the presence of simple electrolytes and at different pH values. Moreover, we studied an equilibrium situation (or one close to it) in contrast to the very dynamic papermaking process. We also tried to generalize the specific problem of the adsorption of cationic starch on cellulose to polyelectrolyte adsorption, a step which has hardly ever been done in paper research.

1.3 Outline of this thesis

In chapter 2 we investigate the adsorption of polyelectrolytes on oppositely charged surfaces with calculations based on a recent polyelectrolyte adsorption theory [18]. It turns out that polyelectrolyte adsorption is a subtle balance of electrostatic and short-range nonelectrostatic interactions. For a given combination of surface charge density, segment charge and nonelectrostatic interactions, this balance can be affected by changing the concentration of simple electrolytes. In an experimental system the effect of salt concentration on polyelectrolyteadsorption can be accurately determined. Hence, from a comparison between model calculations and experimental data, we can gain insight in the balance between electrostatic interactions, which are usually known best and the, mostly unknown, nonelectrostatic interactions. The characterization of our experimental system, microcrystalline cellulose and cationic starches, as well as the methods we used are described in chapter 3. Chapter 4 deals with the adsorption of cationic amylopectin from waxy maize, the branched starch molecule, on microcrystalline cellulose, and how it is affected by changes in electrolyte concentration, changes in type of electrolyte and changes in pH. The trends in the results can be well described with our theoretical model, which of course helps in understanding the adsorption mechanism. The experimental system in chapter 5 is more complicated since it contains cationic potato starch and thus both the linear and the branched starch components, amylose and amylopectin. Again the effects of electrolyte concentration, type of electrolyte and pH are studied, as well as the charge of the polyelectrolyte (degree of substitution) and the competition between amylose and amylopectin. In this case, we can also understand the trends in the adsorption with help of our theoretical model. Finally, in chapter 6, we compare the adsorption behaviour of cationic amylopectin from waxy maize with that of cationic potato starch and we evaluate the use of our experimental and theoretical model systems for the papermaking process.

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2 POLYELECTROLYTE ADSORPTION: A SUBTLE BALANCE OF FORCES

2.1 Introduction

When a polyelectrolyte adsorbs on an oppositely charged surface, it is often found that the adsorbed amount compensates, or slightly overcompensates, the surface charge and that the adsorption increases with increasing salt concentration [1, 2, 3]. At low electrolyte concentration the adsorbed layers are thin and the adsorbed amount hardly depends on molecular weight. This indicates a flat conformation of the polyelectrolyte and these trends refer to highly charged polyelectrolytes. Recent theories on polyelectrolyte adsorption [4, 5, 6] are in agreement with these experimental findings. The somewhat older treatment of Hesselink [7] predicts very thick adsorbed layers, but finds the same effect of increasing salt concentration. The usual argument is that for highly charged polyelectrolytes the repulsion between the segments dominates the adsorption behaviour. At high salt concentration the repulsion is screened, hence the polyelectrolytes behave more like uncharged polymers. They can adopt conformations with loops and tails and the adsorbed amount increases. Naturally, a fully screened polyelectrolyte can only adsorb if there is an attractive interaction between segments and surface which is not electrostatic in nature.

However, sometimes the adsorption of polyelectrolytes is found to *decrease* with increasing salt concentration [8-14], or is not affected at all [8]. In most of these cases the polyelectrolytes have a low charge [8, 9, 12, 13], but highly charged polyelectrolytes can also show this behaviour [10, 11, 14]. Theoretically, decreasing adsorption, or even complete desorption, with increasing salt concentration is considered by Hesselink, Wiegel and Muthukumar [7, 15, 16]. This effect is expected if the attraction between polyelectrolyte and surface is mainly electrostatic in nature, since salt not only screens the segment-segment *repulsion*, but also the segment-surface *attraction*. Thus, in polyelectrolyte adsorption, added salt has two antagonistic effects and it depends on the balance between electrostatic and nonelectrostatic attraction whether or not increasing the salt concentration leads to an increase or a decrease in adsorption. If this force balance is changed, for instance by increasing the segment charge, the influence of the salt concentration can be reversed. Durand et al. [8] found such a reversal for cationic polyacrylamides (copolymers of acrylamide and an acrylate with a quaternary ammonium group) adsorbing on montmorillonite. With a cationic monomer content (τ) of 1% the adsorbed amount decreased with increasing salt

concentration, for τ=5% there was no salt effect, whereas for cationic polyacrylamides with τ=13% and τ=30% the adsorbed amount increased with increasing salt concentration.

Having made these observations, we propose to distinguish two regimes in polyelectrolyte adsorption. We will call them the *screening-reduced adsorption* regime and the *screening-enhanced adsorption* regime. In order to make this distinction operational, we will compare the adsorbed amount in the limit of negligible screening, Γ_0, i.e. at very low salt concentration where the adsorbed amount of polyelectrolyte compensates, or slightly overcompensates, the surface charge, with Γ_∞ the adsorbed amount at very high salt concentration, where electrostatic interactions are virtually eliminated and the polymer can be considered as uncharged. So we have:

1. $\Gamma_0>\Gamma_\infty$, *screening-reduced adsorption.* Electrostatic attraction between segment and surface dominates: the adsorbed amount Γ decreases with increasing ionic strength. Salt can screen this attraction and reduce adsorption.
2. $\Gamma_0<\Gamma_\infty$, *screening-enhanced adsorption.* Nonelectrostatic attraction between segment and surface dominates: Γ increases with increasing ionic strength. Salt can screen the repulsion between the charged segments and enhance the adsorption.

In the intermediate case, when both forces are of roughly equal importance, changing the salt concentration will hardly affect Γ.

In this paper we explore these regimes by numerical calculations based on a recent theory for polyelectrolyte adsorption [6] which is an extension of the Self Consistent Field theory for polymer adsorption by Scheutjens and Fleer [17, 18]. Here, we will only expound the main features of this theory (for technical details the reader is referred to the paper by Böhmer et al. [6]). The polymers are considered to be flexible linear chains in a solution, which is modelled as a lattice. Each lattice site is either occupied by a cluster of solvent molecules, or by a hydrated ion or a polymer segment. The nonelectrostatic energy for interaction between pairs of components is expressed through Flory-Huggins χ parameters. The nonelectrostatic interaction of a component i with the surface (S) is described formally by a similar χ_{iS} parameter. In the mean field approach charges on the surface and on the polymer are smeared out in layers parallel to the surface. The charges are located in a plane in the center of each layer and the space between these planes is free of electrical charges. The electrical potential in every plane is obtained by solving a discrete version of the Poisson-Boltzmann equation. The potential difference between the equidistant planes then depends on the charge on

each plane, on the separation distance (d) between the planes and on the dielectric constant. However, for a surface potential of 100 mV, the potential decay for various values of d calculated with this model, completely coincides with that calculated from the Gouy-Chapman theory [3]. Only if volume exclusion effects play a role, namely for very high surface potentials and at high salt concentrations, does the value of d affect the potential decay [6]. The dielectric constant in a lattice layer changes according to the composition of this layer and is taken to be a linear combination (volume fraction weighted) of the dielectric constants of the polyelectrolyte, salt and water.

The configuration of a polyelectrolyte molecule can be modelled as a step-weighted walk in the lattice. The weighting factors for each step contain the nearest-neighbour contact energy (Flory-Huggins), the electrical potential and the mixing entropy. The mixing entropy accounts for the fact that the probability of a step towards a given lattice layer, decreases as the segment concentration in this layer becomes higher. From all these weighted walks the volume fraction profile and the adsorbed amount are calculated.

One might argue that the mean field approximation is a drawback of this model. Especially for polymers with a low charge density the local electrical potential may differ significantly from the average value. However, the model reproduces many experimental features quite well, so we believe the mean field assumption to be acceptable.

In this paper we restrict ourselves to the adsorption of polyelectrolytes on oppositely charged surfaces and we investigate the effects of salt concentration, segment charge, surface charge density and nonelectrostatic interactions on the adsorption. First we consider the effects of salt concentration, segment charge and surface charge density for cases with electrostatic interactions only (pure electrosorption). Then we treat cases where the segments adsorb specifically and we investigate how the force balance is affected by changing the salt concentration, the strength of the nonelectrostatic attraction, the segment charge and the surface charge density. Finally, we examine the effect of specific adsorption of counterions. We compare our theoretical results with reported experimental results, where possible.

2.2 Results and discussion

2.2.1 Parameters used in the calculations

Calculations were performed using a hexagonal lattice with a layer spacing d of 0.6 nm, which is about the diameter of a hydrated ion. In the

model calculations all concentrations are expressed in volume fractions. In experimental systems, concentrations of the small ions are usually given as molarities and here we will do the same. For conversion of volume fractions to concentrations, the lattice cell volume, determined by the value of d, is necessary [6]. Since we allow only one ion per lattice site, the value of d should not be too high in order to avoid ions filling the complete lattice at high salt concentration. The multiplication factor to convert volume fractions to concentrations is 4.85 for d=0.6 nm [6].

The surface charge was always negative and it was kept constant. In this paper the surface charge density is usually given in C/m^2, but it can be converted to unit charges per lattice site multiplying with 2.25. The calculations presented here were all performed for polyelectrolytes with 100 segments, but the trends were the same for longer chains. The model polyelectrolytes are polyions with a fixed number of unit charges per segment τ and a relative dielectric constant of 20. The relative dielectric constants of all other components were taken as 80. The results of the calculations are not sensitive to the exact value of the dielectric constants, since the bulk volume fraction of the polyelectrolyte, which was kept constant at 1000 ppm, is low. The Flory-Huggins χ parameters for the interaction between ions and solvent molecules were taken to be zero. The interacting molecules behave like hard spheres if χ=0. They do not have short-range interactions, only excluded volume effects play a role; by definition χ=0 for molecules of the same kind and $\chi_{ij}=\chi_{ji}$ [19]. The χ values for the interaction between polyelectrolyte segments and solvent or salt ions, were taken at 0.5. For uncharged polymers χ=0.5 indicates a θ-solvent.

For the nonelectrostatic interaction of a polymer segment P and a solvent molecule O with the surface S, similar Flory-Huggins parameters can be defined. Throughout this paper, however, we will use the adsorption energy parameter χ_s, defined by Silberberg [20] as $-(u_A-u_O)/kT$, where u_A is the adsorption energy of a polymer segment or a salt ion and u_O that of a solvent molecule, k is Boltzmann's constant and T the absolute temperature. Thus, χ_s is positive if A adsorbs preferentially from the solvent. The relation between the Flory-Huggins parameters χ_{AS} and χ_{OS}, and χ_s is $\chi_s=-\lambda_1(\chi_{AS}-\chi_{OS})$, since only a fraction λ_1 (0.25 in a hexagonal lattice) of an adsorbed segment is in actual contact with the surface, so $u_A/kT=\lambda_1\chi_{AS}$ and $u_O/kT=\lambda_1\chi_{OS}$. In our calculations χ_s for the solvent and for the salt ions was zero. In the last section, where we will investigate the effect of specific adsorption of counterions, the χ_s of the salt cation was larger than zero. To distinguish between the adsorption energy

parameter of counterions C^+ and that of polymer segments, we use χ_{sC} and χ_s, respectively.

2.2.2 *Pure electrosorption*

In order to obtain a good insight in the effect of the electrostatic interaction, both the attraction between polyelectrolyte and surface and the repulsion between the segments, we first examine the adsorption Γ (expressed in equivalent monolayers) of a polyelectrolyte which has only electrostatic interactions with the surface (χ_s=0). The effects of the salt concentration and the segment charge τ are shown in figure 1a. The adsorbed amount at very low salt concentration, Γ_0, is always higher than the adsorbed amount at high salt concentration, Γ_∞, which even drops down to zero. At high salt concentration the range of the electrostatic interaction becomes smaller, i.e. the attraction between polyelectrolyte and surface is screened. Since the salt ions have a finite volume, the cations also compete with the polyelectrolyte for adsorption sites on the surface. The polyelectrolyte desorbs if the salt cations are more effective in compensating the surface charge. Therefore, we are clearly dealing with the *screening-reduced adsorption* regime. This behaviour was experimentally found for cationic polyacrylamide adsorbing on silica [10], for cationic polyacrylamide adsorbing on montmorillonite [8] and also in some other systems [11, 12, 13, 14].

Although the uncharged (τ=0) polymer does not adsorb, since it has no adsorption energy to overcome the loss in conformation entropy, a small charge per segment (τ=0.005) suffices to make the polymer adsorb, at least at low salt concentration. The adsorbed amount decreases very quickly with increasing salt concentration. A polyelectrolyte with τ=0.015 has a much higher adsorbed amount at low salt concentration, but the adsorption also decreases with increasing ionic strength. Polyelectrolytes with higher charges per segment adsorb less at low salt concentration, but stay attached to the surface up to higher salt concentration. It is clear that changing τ can have a dramatic effect on the adsorbed amount. Some experimental evidence for this large effect of τ on the adsorption behaviour of a strong polyelectrolyte is available [8, 9, 10]. It also emerged from a recent study about the pH effect on the adsorption of a weak polyelectrolyte [21].

The increase in adsorbed amount when going from τ=0 to τ=0.015, followed by a decrease in adsorbed amount with further increasing τ, is more clearly depicted in figures1b and 1c, where the adsorbed amount is plotted as a function of τ, for different salt concentrations. The sharpest peak occurs at very low salt concentration. At the right side of the peak

the adsorbed amount decreases with increasing segment charge, due to charge compensation. This has been called "1:1 charge stoichiometry" between charges on the adsorbed polyelectrolyte and the total amount of charged groups on the surface (Wågberg et al. [22, 23, 24]). If τ is high less polyelectrolyte is needed to compensate the surface charge density. No more polyelectrolyte than necessary for charge compensation is adsorbed, due to repulsion between the segments. Hence, Γ is given by $\Gamma \cdot \tau = |\sigma_0|$ (σ_0 in unit charges/lattice site), so a hyperbolic curve is obtained with $\Gamma \propto \tau^{-1}$ if σ_0 is constant. The dotted lines in figures 1b and 1c represent this relation. For very low τ, the surface charge is only partly compensated, since the affinity of the polyelectrolyte for the surface decreases with decreasing τ and disappears if $\tau=0$. In this case the adsorption affinity of the macro-ion is so low that it can no longer compete with the small counterions. The maximum, at low salt concentration, seems to occur when the total charge on the chain becomes of order unity, i.e. $\tau \propto r^{-1}$, where r is the chain length, since then the affinity of the macro-ion is comparable to that of the small ions. We also notice that the position of the maximum moves towards higher τ with increasing salt concentration. The polyelectrolyte needs more affinity for the surface, thus a higher charge, to enable compensation of the surface charge and to compete effectively with the counterions. Hesselink also predicted [7] a maximum in the adsorbed amount, which he expected to occur for $\tau \approx 0.1$ at a salt concentration of 0.01 M, i.e. about the same as we found (figure 1c).

A maximum in the adsorbed amount as a function of the segment charge was experimentally found by Wang and Audebert [10] and Durand et al. [8, 9] for the adsorption of cationic polyacrylamide on, respectively, silica and montmorillonite, and also by Tanaka et al. [25] and McKenzie [26] for the adsorption of, respectively, several polyelectrolytes and cationic starch on cellulose. In the above mentioned data of Wang and Audebert [10] and Tanaka et al. [25], the maximum occurred at $\tau \approx 0.01$ for a very low electrolyte concentration (no added electrolyte). Blaakmeer et al. [21] found a maximum in the adsorbed amount of polyacrylic acid adsorbing on a positively charged latex as a function of pH. Again the maximum occurred when the degree of dissociation of the PAA was approximately 0.01. The effect of the salt concentration was studied by Durand et al. [8] for only five values of τ. The adsorbed amount was maximal if τ was 0.01, for all salt concentrations, which differs from our model calculations in figures 1b and 1c. However, this contradiction is caused by the fact that in their system χ_s was larger than zero. Our model

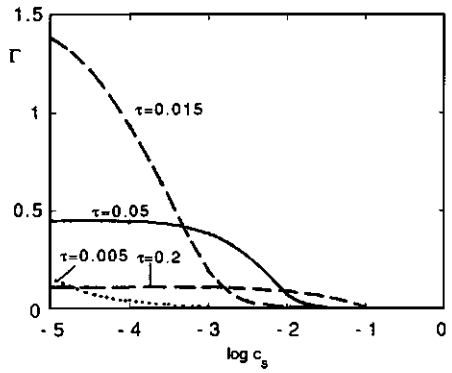

Figure 1a. Effect of segment charge τ on the adsorption of a fully dissociated polyelectrolyte of 100 segments on an oppositely charged surface (–0.01 C/m^2) as a function of the 1:1 electrolyte concentration c_s (M). The adsorbed amount Γ is given in equivalent monolayers.

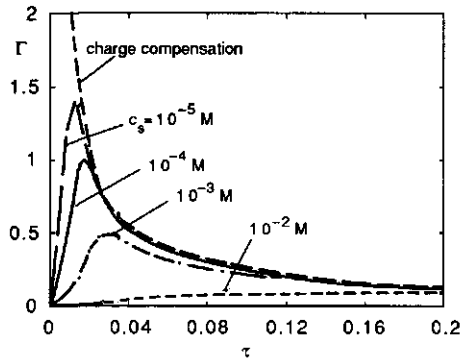

Figure 1b. The adsorbed amount Γ as function of the segment charge τ at four different salt concentrations. The dotted line represents the adsorbed amount necessary for charge compensation.

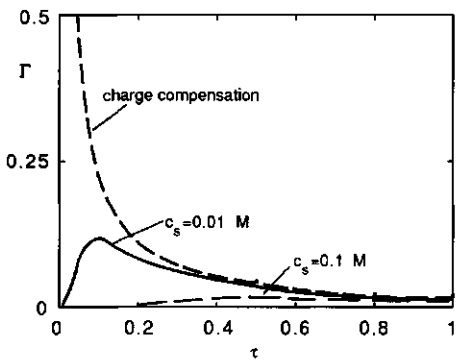

Figure 1c. Essentially the same graph as figure 1b, with different scales for both axes. The adsorbed amount Γ as a function of the segment charge τ at two different salt concentrations.

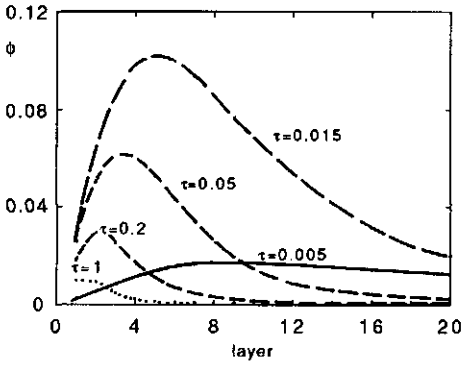

Figure 1d. The volume fraction profile for various segment charges, $c_s=10^{-5}$ M. Other parameters as in figure 1a.

calculations for polyelectrolytes with $\chi_s>0$, in figure 4a, agree very well with the results of Durand et al., as will be discussed in section 2.2.3.

The change in conformation of the adsorbed polyelectrolyte with increasing τ, at low salt concentration, is displayed in figure 1d. At very low values of τ, the polyelectrolyte is hardly attached to the surface, long loops and tails dangle in the proximity of the oppositely charged surface. The layer with the highest volume fraction of polyelectrolyte segments

lies far from the surface. Increasing the segment charge leads to a sharper peak in the volume fraction profile, which lies closer to the surface. If τ=1, the volume fraction of polyelectrolyte is highest in the first layer, so the conformation becomes rather flat. It is obvious that at low salt concentration polyelectrolytes do not always adsorb in a flat conformation. They can even be depleted from the first layer(s), which is due to the long range of electrostatic interactions. The polyelectrolyte does not have to adsorb in the first layer to gain adsorption energy, since adsorption in layers further away from the surface is also energetically favourable. With many segments in the first layer, the polyelectrolyte would loose too much conformation entropy. From an entropic point of view a conformation with long loops and tails is the most favourable. At higher salt concentrations the conformation of polyelectrolytes becomes more extended, irrespective of τ (not shown), since an increasing amount of segments is displaced from the surface by salt cations. Eventually the last segment is detached and the polyelectrolyte desorbs. We will come back to this desorption later.

The next variable we will consider is the surface charge density. As in the case of the segment charge, for all surface charges the adsorption decreases with increasing salt concentration (figure 2a). Γ_0 has a finite value whereas Γ_∞=0, so we are still in the *screening-reduced adsorption* regime. Increasing the surface charge density leads to an increase in the adsorbed amount because polyelectrolytes adsorb until they compensate the surface charge, so $\Gamma=\sigma_0/\tau$, as discussed earlier. Consequently, the adsorbed amount varies linearly with the surface charge at different salt concentrations, provided it is not so high that the polyelectrolyte can not adsorb anymore. In figure 2b we show how Γ varies with the relative segment charge at different surface charges. As in figure 1c, a maximum occurs which moves towards higher τ if the surface charge density is increased, meaning that the polyelectrolyte needs higher affinity, hence a higher τ, in order to be able to compensate the surface charge. On the right hand side of the maximum, the polyelectrolyte is able to compensate the surface charge, whereas on the left hand side the affinity for the surface decreases to zero for the uncharged polymer.

From the segment density profile in figure 2c we can see that at the lowest surface charge densities the volume fraction of the polyelectrolyte in the first layer is lower than in the second layer, indicating a fairly extended conformation. At higher surface charge density, the volume fraction in the first layer is the highest, so the larger electrostatic attraction forces the polyelectrolyte into a flatter conformation, or, to put

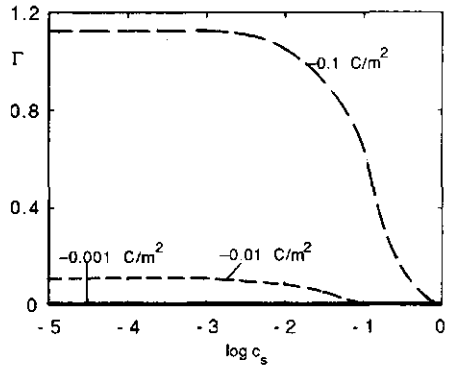

Figure 2a. The effect of surface charge density on the adsorption of a polyelectrolyte of 100 segments with τ=0.2 and χ_s=0, on an oppositely charged surface as a function of the salt concentration c_s (M).

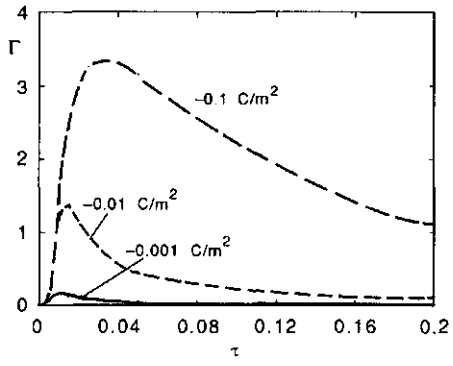

Figure 2b. The adsorbed amount Γ as function of the segment charge τ for three different surface charge densities at $c_s=10^{-5}$ M. For τ>0.2 the adsorbed amount equals the amount required for charge compensation at all three surface charges (not shown). Other parameters as in figure 2a.

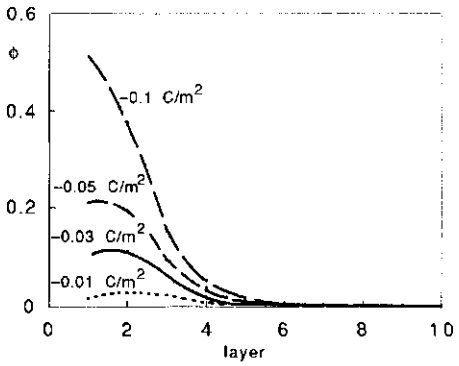

Figure 2c. Volume fraction profile for different surface charge densities, $c_s=10^{-3}$ M. Other parameters as in figure 2a.

it another way, at high potentials the energy gain of adsorption in the first layer is enough to compensate the loss in conformational entropy.

As we have seen in figures 1a and 2a, a polyelectrolyte can be displaced from the surface by salt ions. The salt concentration where the adsorption vanishes, which we call the *critical* salt concentration c_{sc}, seems to depend on the segment charge τ and the surface charge density σ_0, since c_{sc} is larger if τ or σ_0 are larger. A polymer (either charged or uncharged) is desorbed if the adsorption energy no longer compensates the loss in conformational entropy. This means that the net adsorption energy has to

be larger than a critical value, χ_{sc}. From the definition of χ_s (see 2.2.1) for an uncharged polymer it is clear that we are dealing with an *exchange* energy. Attachment of a polymer segment to the surface is accompanied by displacement of solvent molecules, or of other molecules such as salt ions, from the adsorption sites. Desorption occurs if the adsorption energy of molecules other than those from the solvent, *displacers*, is large enough to decrease the adsorption energy of a polymer segment below χ_{sc} [27, 28]. In polyelectrolyte adsorption we also have to take into account the electrostatic interactions. Salt ions can, therefore, act as displacers for a polyelectrolyte even if their "chemical" interaction with the surface is negligible.

An analysis of the criteria for electrosorption (χ_s=0) of a polyelectrolyte chain in a salt solution was made by Wiegel [15] and extended by Muthukumar [16] using mean field arguments. For a Gaussian polyelectrolyte without internal repulsion, Wiegel obtained the following relation between the surface charge density σ_0 and the segment charge τ on the one hand and the Debije screening length κ^{-1} on the other hand:

$$|\tau\cdot\sigma_0| \propto \kappa^3 \qquad (1)$$

Wiegel's theory was extended by Muthukumar [16] for flexible polyelectrolytes. Due to internal repulsion, polyelectrolytes are swollen and shrink when the segment-segment repulsion is screened. Therefore, the effect of the salt concentration on the adsorbed amount is smaller. Muthukumar showed that Wiegel's κ^3 has to be multiplied by a factor of $\kappa^{-4/5}$, so

$$|\tau\cdot\sigma_0| \propto \kappa^{11/5} \text{ or } c_{sc} \propto (\tau\cdot\sigma_0)^{10/11} \qquad (2)$$

With our model we calculated at which salt concentration the adsorbed amount of a polyelectrolyte is zero. We determined the critical salt concentration for polyelectrolytes with various segment charges adsorbing on a surface with a charge density of -0.01 C/m^2, and for a polyelectrolyte with τ=0.2 adsorbing on a surface with various charge densities. The relations between c_{sc} and τ, and between c_{sc} and σ_0 were both power laws, with exponents of 0.88 (correlation coefficient>0.9995) and 0.85 (correlation coefficient>0.9999) respectively. Hence, the exponents obtained with the Böhmer model agree very well with 10/11=0.91 of equation (2). This agreement between Muthukumar's analytical theory and the numerical calculations based on the Böhmer theory is to be expected, since both theories use a mean field approach and flexible chains.

We noticed that for absolute surface charge densities larger than 0.02 C/m^2 the double logarithmic plot of c_{sc} as function of σ_0 is not linear anymore. This non-linearity is caused by high potentials, for which the Debije-Hückel approximation can not be used. Muthukumar derived equation (2) using this approximation, whereas in the Böhmer model the exact solution of the Poisson-Boltzmann equation is used. The DH-approximation holds reasonably well for potentials smaller than 50 mV. For the salt concentrations that we are dealing with, the surface potential is about 50 mV at $\sigma_0 \approx 0.02$ C/m^2.

We should note here, that a different relation between c_{sc} and the product of τ and σ_0, was obtained by Evers et al. [29], who used an earlier version of the Böhmer model. Evers et al. studied the adsorption of polyelectrolytes with $\chi_s>0$, and derived a simple expression for the critical surface charge density σ_{0c}, by only considering the electrostatic interactions in the first layer (i.e. within a distance d from the surface). His result was:

$$\sigma_{0c} = \frac{\kappa\varepsilon_0\varepsilon_s kT}{\tau e}(\chi_s + \lambda_1\chi - \chi_{sc}) \tag{3}$$

where ε_0 is the permittivity of vacuum, ε_s the relative dielectric constant of the solvent and e the elementary charge. If one varies ionic strength rather than surface charge density, expression (3) reads:

$$c_{sc} \propto (\tau\cdot\sigma_0)^2 \tag{3a}$$

Now the exponent is 2 instead of 10/11. Hence, equation (3) does not correctly describe the displacement by salt studied here. The assumption that only electrostatic interactions in the first layer need to be considered, is probably not justified. Yet, Evers found a fairly good agreement between equation (3) and his numerical calculations. The reason for this is that he used highly charged (τ=1) polyelectrolytes and χ_s=1. From figures 1d, 2c and 3b it can be seen that a high segment charge, high surface charge density and a not too small nonelectrostatic affinity for the surface ($\chi_s>0$), promote a flat conformation of the adsorbed polyelectrolyte. So, in Evers' calculations, all the segment-surface interactions are indeed short range. The difference of a factor κ^2 between Evers' and Wiegel's analysis, or, equivalently the factor $\kappa^{9/11}$ between the analyses of Evers and Muthukumar, is due to the neglect of adsorbed polyelectrolyte segments that interact with, but do not touch the surface.

2.2.3 *Effect of specific adsorption of segments*

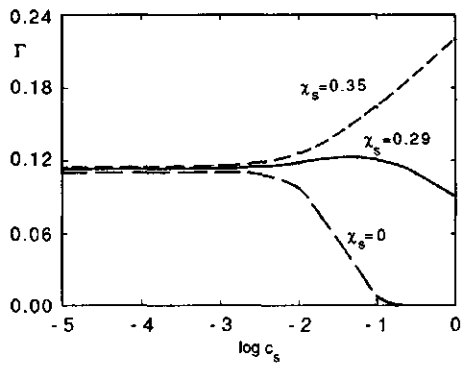

Figure 3a. The adsorbed amount, Γ as a function of the salt concentration c_S (M) for different values of χ_S, the nonelectrostatic interaction with the surface; τ=0.2, σ_0=–0.01 C/m^2.

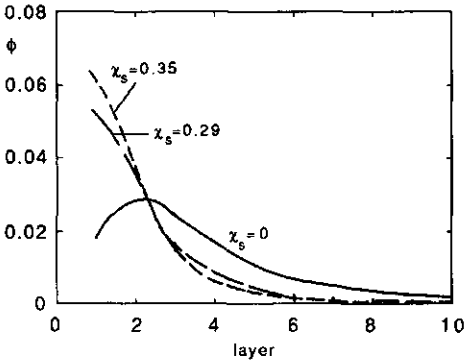

Figure 3b. Volume fraction profile for different values of χ_S; $c_S=10^{-3}$ M. Other parameters as in figure 3a.

In the previous section we have seen that only the *screening-reduced adsorption* regime is found if the interaction between polyelectrolyte and surface is merely electrostatic. The *screening-enhanced adsorption* regime emerges when a non-electrostatic interaction (χ_S) is introduced, as is shown in figure 3a. It is more difficult to desorb the polyelectrolyte with salt if $\chi_S>0$, even for very small χ_S, since a nonelectrostatic attraction is added to the electric attraction. The effect of added salt is already nearly eliminated for the curve in the middle (χ_S=0.29): at first the adsorption increases a little with increasing salt concentration, after which it finally decreases slightly. A modest further increase in χ_S, modifies the behaviour entirely: now the adsorption clearly increases with increasing salt concentration. This is the onset of the *screening-enhanced adsorption* regime. Repulsion between the segments suppresses the adsorption at low salt concentration but screening of this repulsion at high salt concentration leads to development of loops and tails and, therefore, to an increase in the adsorbed amount. From the volume fraction profile (figure 3b) we can see that for $\chi_S>0$, much more polyelectrolyte is present in the first layer, because the polyelectrolyte only gains the nonelectrostatic adsorption energy when adsorbing in the first layer. For the conformation of a polyelectrolyte at the surface, therefore, it is quite important whether or not a nonelectrostatic attraction between polyelectrolyte and surface exists.

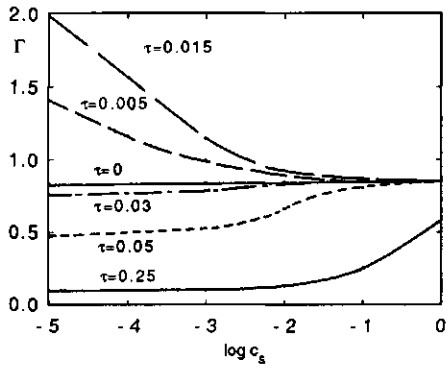

Figure 4a. The adsorbed amount Γ as function of the salt concentration c_S (M) for different values of the segment charge τ. χ_S=0.6 and σ_0=–0.01 C/m^2.

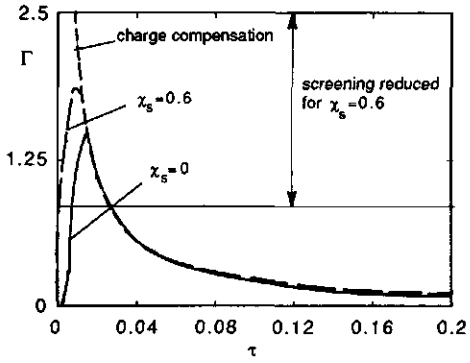

Figure 4b. The adsorbed amount Γ as a function of segment charge τ for χ_S=0 and χ_S=0.6 at c_S=10^{-5} M; σ_0=–0.01 C/m^2 in both cases. The horizontal line in the graph is drawn at the level of the adsorbed amount for an uncharged polymer with χ_S=0.6.

The balance between nonelectrostatic and electrostatic attraction can be varied by changing χ_S, which however, is not easily accomplished in an experiment. Usually it is easier to change the segment charge or the surface charge density, and this may serve the same purpose. In figure 4a it can be seen how varying τ affects the influence of the salt concentration. First of all, the uncharged polymer is also adsorbed; its adsorbed amount is hardly affected by the salt concentration. Then, a

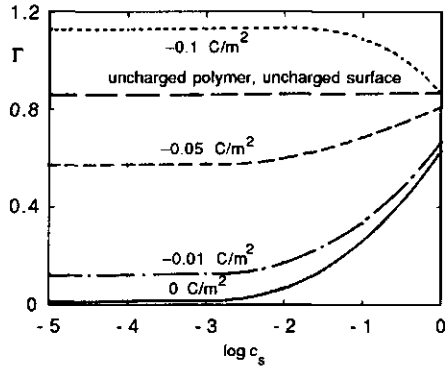

Figure 5. The adsorbed amount Γ as a function of the salt concentration c_S (M) for different values of the surface charge density. χ_S=0.6; τ=0.2.

gradual increase in a segment charge τ takes us through the *screening-reduced adsorption* and into the *screening-enhanced adsorption* regime. Notice that the adsorbed amount of the polyelectrolytes at high salt concentration does not always completely reach that of the uncharged polymer, although χ_s is the same for all values of τ ($\Gamma(\tau=0)=\Gamma_\infty$).

In figure 4b we can see how changing τ affects Γ for $\chi_s=0$ (see also figure 1c) and $\chi_s=0.6$ respectively. Both curves show a maximum in the adsorbed amount, which for $\chi_s=0$ occurs at $\tau=0.015$, whereas it is slightly shifted to $\tau=0.01$ for $\chi_s=0.6$. The larger adsorbed amounts for $\chi_s=0.6$ than for $\chi_s=0$ in the range $0<\tau<0.01$, are another difference between the two curves. For these small values of τ, the adsorbed amount for a polyelectrolyte is larger than for an uncharged polymer with the same χ_s, since a polyelectrolyte also gains adsorption energy for segments in layers further from the surface (figures 1d, 2c and 3b). With figure 4b we can determine where the transition from the *screening-reduced adsorption* to the *screening-enhanced adsorption* regime takes place. The *screening-reduced adsorption* regime occurs if $\Gamma_0>\Gamma_\infty$. If we draw a horizontal line at the level of Γ_∞, the adsorbed amount of the uncharged polymer at $\chi_s=0.6$, we are dealing with the *screening-reduced adsorption* regime for all values of τ smaller than that at the intersection point of the curve and the line: $\tau=0.03$. The salt concentration will hardly affect the adsorbed amount for $\tau=0.03$ because $\Gamma_0\approx\Gamma_\infty$. It should be noted that if $\chi_s>0$, charge reversal can take place. This is not yet the case in figure 4b, since for $\chi_s=0.6$ the adsorbed amounts are equal to those necessary for surface charge compensation. This transition of the *screening-reduced adsorption* to the *screening-enhanced adsorption* regime with increasing segment charge was experimentally found by Durand et al. [8] for the adsorption of cationic polyacrylamide on montmorillonite. In figure 5, where the surface charge density is varied, the same trends can be observed as in figure 4. Now the *screening-reduced adsorption* regime emerges for the highest surface charge density ($\sigma_0> \tau\cdot\Gamma_\infty$, with σ_0 in elementary charges/lattice site) and the *screening-enhanced adsorption* regime for the lower surface charges. At high salt concentration the adsorbed amounts move towards the adsorbed amount of the uncharged polymer, but they do not reach this value completely. The adsorbed amount again increases linearly with increasing surface charge density. The effects of electrostatic and nonelectrostatic attraction are additive, as was also found before by van der Schee and Lyklema [4], Papenhuijzen et al. [5] and Evers et al. [29] in their model calculations. This linear increase is confirmed by experiments, for instance by Bonekamp [3, 30].

2.2.4 *The boundaries of the regimes*

In this section we will explore the boundaries of the regimes more systematically. As we have seen before, the *screening-reduced adsorption* regime occurs if $\chi_s \leq 0$ for all values of τ and σ_0. Neglecting charge reversal, the *screening-reduced adsorption* regime occurs for $\chi_s > 0$, in first approximation, if $\tau < \sigma_0/\Gamma_\infty$ (with σ_0 in elementary charges/ lattice site). In figure 6 the boundaries between the regimes are shown for three different values of χ_s and various values for τ and σ_0. The first diagram is for $\chi_s = 0.29$, which is approximately equal to the critical value χ_{sc}, necessary to make an uncharged polymer adsorb at all, whereas for χ_s values larger than 4 the adsorbed amount of an uncharged polymer hardly increases anymore. The reason is that if the layer closest to the surface is completely filled with segments, the adsorbed amount (at fixed chain

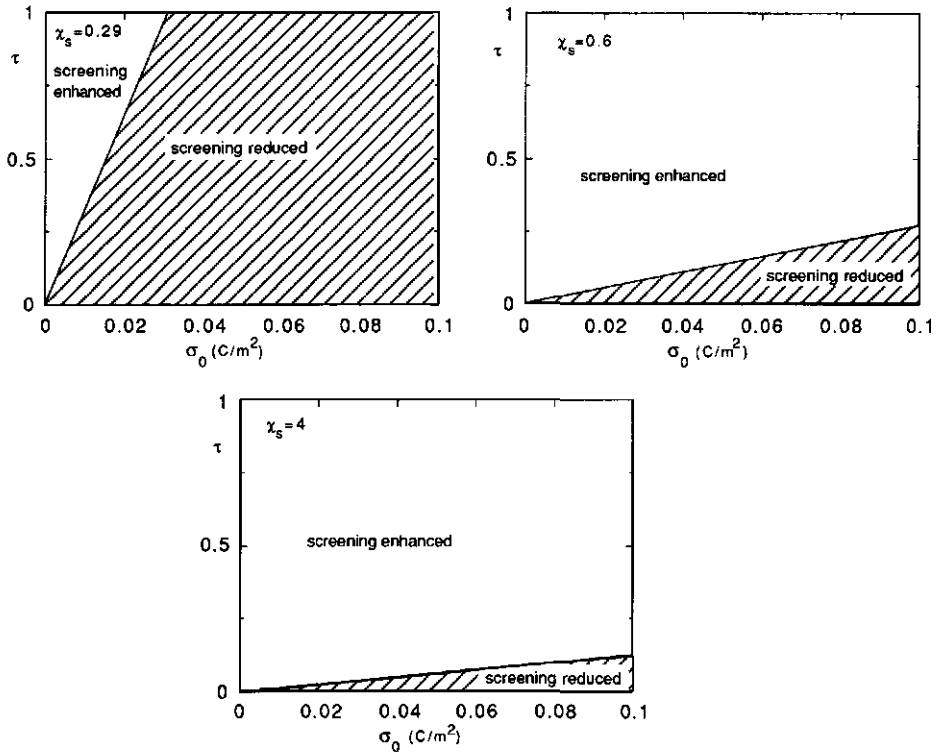

Figure 6. Values for τ and σ_0 for different χ_s (as indicated in the figure) where the *screening-reduced adsorption* regime and *screening-enhanced adsorption* regime occur for a polyelectrolyte with 100 segments.

length) cannot increase anymore [17]). From figure 6 it is clear that the *screening-reduced adsorption* regime will emerge for a broad range of τ if χ_s is small or if σ_0 is large, whereas for large χ_s or small σ_0 it comes out only for very small τ.

It now becomes clear why the *screening-reduced adsorption* regime was not found in earlier calculations based on the mean field model [4, 5, 6]. Only the influence of the salt concentration for highly charged polyelectrolytes (τ=−1) and χ_s>0 (usually χ_s=1) had been calculated. We also understand better why, in experimental systems, the adsorption is more often than not found to increase with increasing salt concentration. Many experiments are done with highly charged polyelectrolytes. The *screening-reduced adsorption* regime for such a system would only be found if the attraction between polyelectrolyte and surface is (almost) purely electrostatic, and it is rather likely that at least some nonelectrostatic affinity between polyelectrolyte and surface exists.

2.2.5 Specific adsorption of counterions

So far we have considered the salt ions as solvent molecules, except for their charge. However, it is well known that salt ions may adsorb specifically, which, in terms of this model, implies that their χ_s is larger than zero. We will investigate the effect of specifically adsorbing salt ions having the same charge as the polyelectrolyte, namely the counterions. The most interesting effect can be expected for the *screening-enhanced adsorption* regime, since the trend for the *screening-reduced adsorption* regime will not change when the salt ions have adsorption energy (the decrease of the adsorption with increasing salt concentration will only be more pronounced). Since the χ_s of the polyelectrolyte is positive, the adsorbed amount will initially increase with increasing salt concentration. Then, at higher salt concentration the salt cations win the competition and start displacing the polyelectrolyte. The result of these two trends is a *maximum* in the adsorbed amount as a function of the salt concentration (figure 7). The larger the nonelectrostatic interaction of the salt cations C with the surface (the more positive their χ_{sC}) the more effective they act as displacers, so that the maximum becomes less pronounced and moves towards lower concentrations. A maximum in the adsorbed amount as a function of salt concentration has occasionally been found experimentally. For instance by Bonekamp [3, 30] for polylysine on silica, by Lindström & Wågberg [31] and Tanaka et al. [25] for respectively, cationic polyacrylamides and polyDMDAAC (DiMethyl-DiAllylAmmonium Chloride) on cellulose fibers, and by van de Steeg (chapter 4 of this thesis) for cationic amylopectin adsorbing on microcrystalline cellullose.

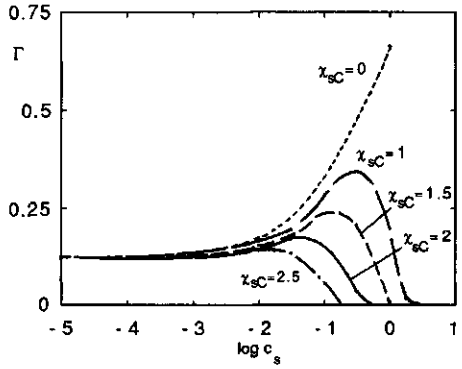

Figure 7. The adsorbed amount Γ as a function of the salt concentration c_s (M) for a polyelectrolyte of 100 segments with τ=0.2 and χ_s=0.6, on an oppositely charged surface (-0.01 C/m^2). The short-range, nonelectrostatic interaction of the salt cation C^+ with the surface, χ_{sC}, is varied.

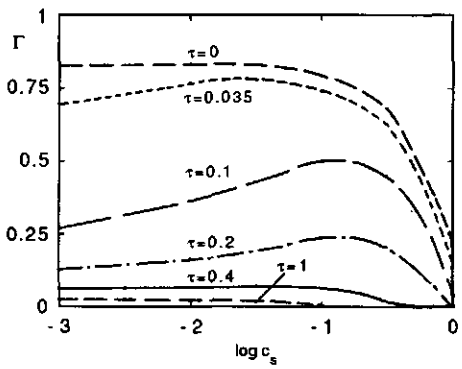

Figure 8. The adsorbed amount Γ as a function of the salt concentration c_s (M) for a polyelectrolyte with χ_s=0.6 and a specifically adsorbing salt cation C^+ with χ_{sC}=1.5. The segment charge τ of the polyelectrolyte is varied, σ_0=-0.01 C/m^2.

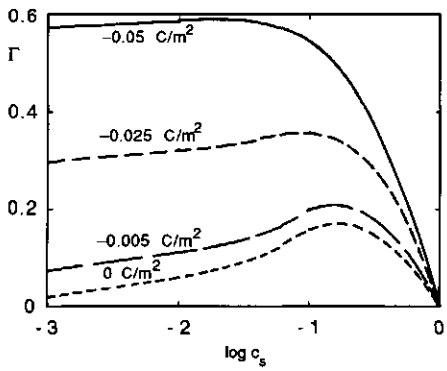

Figure 9. The adsorbed amount Γ as a function of the salt concentration c_s (M) for various surface charge densities, τ=0.2, χ_s=0.6 and χ_{sC}=1.5.

In figure 8 the segment charge τ is varied at constant surface charge density, χ_s and χ_{sC}. Surprisingly, the critical salt concentration decreases with increasing segment charge. This effect is opposite to what has been found when only electrostatics play a role (for instance figure 1a, see also equation 2). The reason is that specifically adsorbing salt ions are localized in the first layer, because otherwise they cannot gain the extra adsorption energy. A polyelectrolyte with a high segment charge also has a preference for the first layer (see figure 1d), so that the displacement of

a polyelectrolyte with high segment charge by salt ions with adsorption energy is more effective.

Figure 9 shows that the maximum gradually disappears with increasing surface charge density. The reason is that the *screening-reduced adsorption* regime is approached. The adsorbed amount is proportional to the surface charge (for salt concentrations below the critical value).

2.3 Conclusions

Although it has been emphasized more than once that, at low salt concentration, polyelectrolytes adsorb in a flat conformation and that the adsorption increases with increasing salt concentration, we have shown this picture to be incomplete. We propose to distinguish two regimes based on the adsorption behaviour of the polyelectrolyte upon increasing salt concentration, the *screening-enhanced adsorption* and the *screening-reduced adsorption* regime. In the former the adsorption increases with increasing salt concentration, because the dominating effect is screening of the repulsion between the segments. In the latter the adsorption decreases with increasing salt concentration, since the screening of the attraction between polyelectrolyte and surface dominates. Whichever regime emerges for a specific combination of polyelectrolyte and oppositely charged surface depends on the balance of electrostatic and non-electrostatic attraction between polyelectrolyte and surface. The strength of this electrostatic interaction is determined by the charges of the segments and the charge density on the surface.

If the attraction between polyelectrolyte and surface is purely electrostatic (χ_s=0) we are always in the *screening-reduced adsorption* regime. The polyelectrolyte can be displaced from the surface by salt ions. The critical salt concentration, the concentration where the adsorption vanishes, is found to scale as $\sigma_0^{0.86}$ and $\tau^{0.88}$ respectively. These results are in good agreement with the scaling $(\sigma_0\tau)^{10/11}$ predicted by Muthukumar. The conformation of the polyelectrolyte at the surface can be more or less extended, depending on τ. For $\tau<<1$ most segments are not present in the first layer but in layers further away from the surface. This is due to the long range nature of the electrostatic attraction, i.e. the polyelectrolyte does not have to adsorb in the first layer in order to gain adsorption energy.

If a short range, nonelectrostatic attraction between polyelectrolyte and surface exists, both the *screening-enhanced adsorption* and the *screening-reduced adsorption* regimes are found. A simple rule is that Γ is reduced by screening whenever $\sigma_0/\tau \geq \Gamma_\infty$. Since Γ_∞ increases monotonously with χ_s,

chain length and χ, one finds the *screening-reduced adsorption* regime only by taking sufficiently high values of σ_0 and/or sufficiently low values of τ. The conformation of all polyelectrolytes, irrespective of τ, becomes flatter if $\chi_s>0$, because this non-electrostatic adsorption energy can only be gained in the first layer.

Most of the predictions of the Böhmer-model discussed here agree very well with experimental results, but some can not be checked since, to our knowledge, no suitable experiments have been published yet. We hope that future will shed more light on the subtle balance of electrostatic and non-electrostatic forces that determines the adsorption behaviour of polyelectrolytes.

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3 MATERIALS AND METHODS

3.1 Cellulose

3.1.1 *Properties of cellulose*

Cellulose is the most abundant of all naturally occurring organic compounds and probably makes up at least a third of all vegetable matter in the world. It is the main constituent of the cell walls of higher plants. Cellulose is a linear polymer of β-glucose, with glycoside bonds between carbon atoms 1 and 4 (figure 1) and may have molecular weights in the order of 10^5 [1, 2]. Since β-glucose has its substituents in equatorial

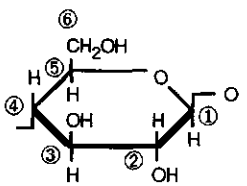

Figure 1. Structure of a β-glucose unit.

position, the hydroxyl groups and the CH_2OH group, the cellulose chains are flat ribbons that can pack together neatly as crystalline bundles. These bundles twine together in hollow cylinders called fibrils, which then form a larger structure, namely cellulose fibers. In fibers both crystalline and amorphous regions occur. The purest natural cellulose is the cotton fiber with 70% crystalline material, as determined by X-ray diffraction, whereas wood cellulose is less crystalline with 65% [1]. Due to the high crystallinity it is difficult to dissolve cellulose. It does not dissolve in pure water; cellulose fibers only swell. Cellulose fibers obtained from wood by a pulping process are still associated with other polysaccharides, which are called hemicelluloses. An indication of the amount of cellulose in wood fibers is the solubility in 17.5% sodium hydroxide solutions at room temperature. The purest form is α-cellulose, the part that does not dissolve. The fraction that dissolves, but precipitates when acidified with acetic acid, is β-cellulose, and γ-cellulose is the non-precipitated dissolved fraction. Most of the hemicelluloses, short chain polysaccharides of a mixture of monosaccharides, are present in γ-cellulose. β-cellulose mainly contains short chain cellulose molecules with degree of polymerization (DP) between 10 and about 200. Cellulose molecules with DP larger than 200 are present in α-cellulose [1, 2, 3].

Cellulose fibers in water carry a negative charge which originates from carboxylate groups. The majority of the carboxylate groups are of uronic

acid type and are bound to the hemicellulose xylan, which is associated with the cellulose fibers. Oxidated hydroxyl groups in the cellulose chains can also contribute to the amount of carboxylate groups [4]. The charge on cellulose fibers at pH≈7 varies from –3 C/g for bleached sulphate pulp, to –10 C/g for unbleached sulphate pulp [5].

In this study microcrystalline cellulose is used as a model for cellulose fibers. Microcrystalline cellulose is mechanically desintegrated level-off DP cellulose [6]. Level-off DP cellulose is the product resulting from the hydrolysis of α-cellulose after 15 min in 2.5 N HCl at 105±1°C. It has an average degree of polymerization (level-off DP) which is not decreased any further by continued hydrolysis under the same conditions. The level-off DP of wood fibers ranges from 140 to 400 [7].

3.1.2 Materials

Microcrystalline cellulose was obtained from Sigma (Sigmacell type 20) with an average particle diameter of 20 μm, according to the manufacturer. Cotton linters (acid washed for column chromatography) with fiber length of 0.02-0.15 mm were obtained from Fluka. Water was pre-purified by reversed osmosis and subsequently passed through a Milipore Super Q apparatus or an Elgastad UHP system. Other chemicals were analytical grade and used without further purification.

3.1.3 The appearance of cellulose: electron micrographs

In figures 2 and 3 electron micrographs of cleaned microcrystalline cellulose (see 3.1.5.2) and cotton linters are shown. The samples were prepared by a solvent-exchange drying procedure, see for instance [8, 9, 10], to keep the pores which are present in water-swollen cellulose (and otherwise collapse upon drying), open. In the solvent-exchange drying procedure cellulose was leached during 4 hours with solvents with decreasing polarity and dried in air afterwards. The ratio of cellulose:liquid was 1:15, and the following solvents were subsequently applied (in brackets the ratio of the liquids):

a. H_2O: 99% ethanol: tertiary butanol (5:4:1)
b. H_2O: 99% ethanol: tertiary butanol (3:5:2)
c. H_2O: 99% ethanol: tertiary butanol (1.5:5:3.5)
d. 99% ethanol: tertiary butanol: amyl acetate (4.5:2:3.5)
e. 99% ethanol: tertiary butanol: amyl acetate (4.5:0.5:5)
f. propylene oxide
g. pentane

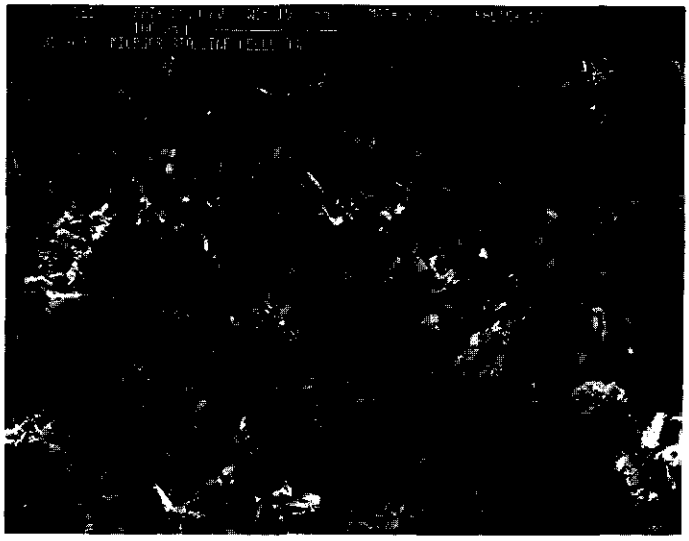

Figure 2a. Electron micrograph of solvent-exchanged and cleaned microcrystalline cellulose powder. The magnification is 250x and the bar indicates 100 μm.

Figure 2b. Electron micrograph of solvent-exchanged and cleaned microcrystalline cellulose powder. The magnification is 2000x and the bar indicates 20 μm.

Figure 3a. Electron micrograph of solvent-exchanged cotton linters. The magnification is 250x and the bar indicates 100 μm.

Figure 3b. Electron micrograph of solvent-exchanged cotton linters. The magnification is 800x and the bar indicates 50 μm.

The microcrystalline cellulose contains fairly large particles resembling fragments of fibers like those in the micrographs of cotton linters. Cellulose microcrystals have another appearance in electron micrographs [6], they are small elongated particles resembling wheat corns. Aggregates of microcrystals, which can be formed during spray drying [6], are a spongy, random fine structure, different from those in our micrographs. However, the electron micrographs in [11] of level-off DP cellulose and cellulose microcrystals clarify what structure we are dealing with. The level-off DP cellulose still looks like fibers with some microcrystals around them, in contrast to the fine, wheat corn like microcrystals. Thus our "microcrystalline" cellulose is actually level-off DP cellulose, instead of cellulose microcrystals. It should be noted that the microcrystals can be obtained from the level-off DP cellulose by applying shear forces to a dispersion of the latter, although even then a fraction of the material remains in the form of unattrited fiber fragments [12]. The surface of our "microcrystalline" cellulose resembles that of the cotton linters and seems rough.

3.1.4 X-ray diffraction

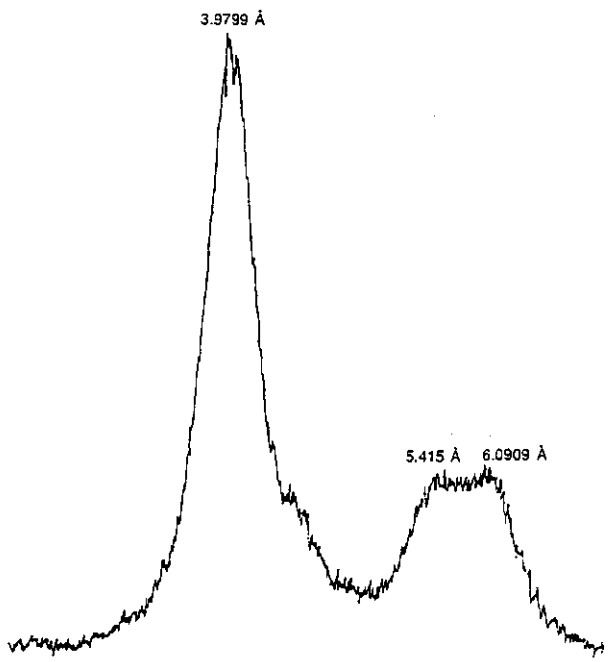

Figure 4. X-ray diffractogram of microcrystalline cellulose powder.

An X-ray diffractogram of our microcrystalline cellulose is shown in figure 4. The position of the peaks corresponds to the distances between glucose units in the cellulose unit cell [13] (figure 5): 3.98 Å for 002, 5.42 Å for $10\bar{1}$ and 6.09 Å for 101. The peaks are fairly sharp, which means that the amount of crystalline material is rather large. Very sharp peaks are only obtained for completely crystalline samples, so the broadening of the peaks indicates that our sample still contains some amorphous material.

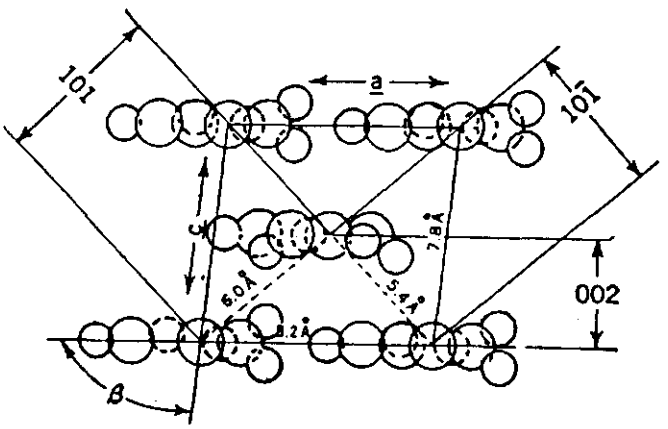

Figure 5. View down *b* axis of unit cell of native cellulose showing the location of *a* and *c* axes, angle β, and the (101), ($10\bar{1}$), and (002) planes [13].

3.1.5 Hemicelluloses

3.1.5.1 Hemicelluloses in microcrystalline cellulose

From the determination of starch with sulphuric acid and phenol [14] for the measurement of adsorption isotherms of cationic starch on microcrystalline cellulose, an unexpected problem emerged: the blanks also contained carbohydrate. Cellulose was unlikely to be the cause, since the wavelength of the absorbance maximum was around 480 nm. Hexoses like glucose have λ_{max}=490 nm [14], whereas pentoses have a maximum at 480 nm. Hemicellulose can be the source of pentoses because a commonly occurring type contains the pentose xylose. In the cell wall cellulose is associated with other polysaccharides, also called hemicellulose, and this is still so after pulping. In wood chemistry these polysaccharides are referred to as "xylose" and "mannose", which does not imply homogeneous polymers of anhydroxylose or anhydromannose, but only indicates that the respective sugars, or derivates thereof, may be detected after complete hydrolysis to monomeric units [3]. Even α-

cellulose, the raw material for microcrystalline cellulose, contains hemicellulose [3].

The amount of carbohydrate in the supernatant (10 min 4400*g*) of a 40 g/l suspension of microcrystalline cellulose, depended on salt concentration and pH. With water about 70 mg/l carbohydrate was extracted, but with 0.2 M NaCl only 20 mg/l. This effect of salt is consistent with the observation of Ström et al. [15], that the adsorption of xylan on cellulosic fibers increases with increasing NaCl concentration. At pH=10 four times as much carbohydrate was found in solution as at pH=3, which very clearly points in the direction of hemicellulose since hemicelluloses are, by definition, the polysaccharides extracted from cellulose or cell wall material with alkaline solutions or water. Both pH and salt dependence were found for the dissolution of carbohydrates during beating of kraft pulps by Lindström et al. [16].

Microcrystalline cellulose (MCC) powder and an aqueous extract from MCC were analysed on their monosaccharide composition by Seaman hydrolysis [17] and conversion to their alditol acetates as described by Englyst and Cummings [18]. In table 1 we can see that the MCC powder contains 2-3% monosaccharides other than glucose. The hemicellulose content of MCC is at least the same, but is higher if the hemicelluloses also contain glucose, like in glucomannan. Besides glucose, in the extract from MCC powder with 2 mM NaCl, only xylose occurs (see table 1). It is more often found that xylans are better extractable with water than hemicelluloses containing mannose [19]. Usually the amount of hemicellulose extractable with water is small. Huffman [20] reported extraction of as little as 1 g of a hemicellulose containing 35% xylose, from 1 kg of the paper used for separating mixtures of sugars. The amount of water extractable xylans increases when cellulose fibers are ground [19]. Lindström et al. [16] found that kraft pulps released considerable amounts of carbohydrates, especially xylans, when they were beaten in water. Perhaps the treatment of cellulose with acid to prepare

Table 1. Analysis of microcrystalline cellulose (MCC) powder and an aqueous extract.

sample	monosaccharide analysis			
	% xylose	% mannose	% glucose	% total
MCC powder	1.4	1.4	97.2	100
extract*	80.9	–	19.1	100

*from 10 ml freeze dried supernatant (10 min. 4400*g*) of 40 g/l MCC powder in 2 mM NaCl, shaken for 1.5 hours.

microcrystalline cellulose makes it easier to extract hemicelluloses with water.

3.1.5.2 Cleaning procedure

The concentrations of carbohydrates in the aqueous extracts, the blanks of our adsorption isotherms, were ±50 mg/l, so only 10% of the xylose in MCC can be extracted by 2 mM NaCl. However, this tiny concentration has an absorbance of about 1 in the sulphuric acid-phenol method [14], hence, in order to get rid of this high "blank", we had to find a way to remove as much of the hemicellulose as possible. Alkaline extraction of MCC seemed the most effective way to do this. Hamilton and Quimby [21] recommended extracting several times with 5% NaOH, a higher concentration could degrade the cellulose. We adopted the following procedure.

> In 250 ml of 5% NaOH 25 g MCC was shaken for 20 min and after centrifugation (5 min 6650*g*) a fresh aliquot of the NaOH solution was added. The cellulose was stirred up and the dispersion was again shaken for 20 min. This was repeated four times. Then the MCC was washed four times with water. An amount of 0.1 M HCl large enough to decrease the pH from 12 to 7 (typically 6-7 ml) was added. Again the MCC was washed three times with water, ensuring that the conductivity of the supernatant was less than 5 µS/cm. The cleaned MCC was freeze-dried.

The extraction was monitored by a carbohydrate determination of each fraction with the sulphuric acid-phenol method (figure 6). The largest

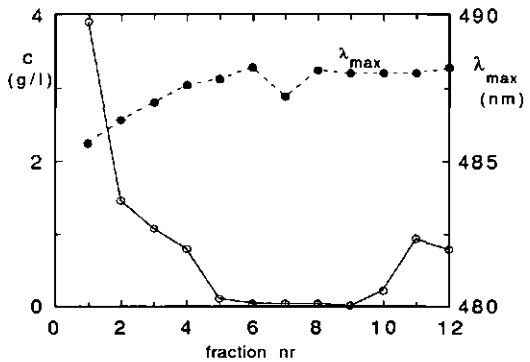

Figure 6. The carbohydrate concentration (left axis) of every fraction in the cleaning procedure of microcrystalline cellulose (description see text). The wavelength of maximum absorbance of the fractions, in the carbohydrate determination is also indicated in the graph (axis on the right hand side).

amount of carbohydrate is extracted in the first four fractions (5% NaOH), which contain pentoses, as can be seen from the wavelengths of their absorbance maxima. The last fractions (washing of the neutralised sample with water), contain a higher amount of carbohydrates than the preceding fractions, with wavelengths of absorbance maxima close to 490 nm. These fractions were cloudy and probably contain a sol of cellulose micro-crystals. Addition of salt leads to flocculation of the sol. The total amount of carbohydrates extracted from 100 g MCC was 1500 mg (6%, fractions 1 to 7) plus 390 mg (1.5%, fractions 8-10), which is 7.5% in total. After the washing procedure, only about 5 mg/l carbohydrates (at 2 mM NaCl) could be extracted from 40 g/l MCC, which means that the absorbance of the blank measured by the sulphuric acid-phenol method was acceptable, namely about 0.1.

3.1.6 Potentiometric titrations

Potentiometric titrations were performed with an automatic titration setup [22]. After each addition of acid or base, a maximum equilibration time of 15 min was allowed. Ten grams of cellulose in a volume of 300 ml were titrated with 0.05 M HNO_3 and 0.05 M KOH. Each titration cycle started with addition of acid in 2 mM KNO_3. After two acid and two base titrations, salt was added and this was repeated until titrations in 2 mM, 0.01 M, 0.05 M, 0.2 M and 1 M KNO_3 had been performed in the same solution. Salt solutions (blanks) were titrated the same way. In order to minimize the amount of CO_2 in the solution, freshly boiled water was used throughout, N_2 was bubbled through the sample and the acid titration was performed first.

For calculations the second acid titration was used. The change in surface charge per unit weight $\Delta\sigma_0$ at a certain pH was calculated as follows, after correction for the volume difference between blank and suspension:

$$\Delta\sigma_0 = \frac{\Delta mol H^+ \cdot F}{m} = \frac{\Delta V \cdot c \cdot F}{m} \qquad (1)$$

were $\Delta mol\ H^+$ is the amount of protons released or adsorbed by cellulose, F is the Faraday constant, ΔV is the difference in volume of acid added to obtain a certain pH between the blank and the cellulose dispersion in l, c is the concentration of the HNO_3 or KOH solution in moles/l, and m is the amount of cellulose in grams. Since the charged groups on cellulose are only carboxylate groups [4], there is no point of zero charge in the pH range of our titrations so, strictly speaking, we do not know the absolute charge. The position of the titration curves relative to each other was

determined in a separate experiment. We measured the pH of a dispersion of 10 grams cellulose in 300 ml 2 mM KNO_3 (pH≈7), added salt to a concentration of 0.01 M and measured the pH again. This was repeated for 0.05, 0.2 and 1 M KNO_3. From the change in pH due to addition of salt (concentration a, before and concentration b after addition) the amount of released protons could be calculated:

$$\Delta\sigma = \frac{\Delta mol H^+_{a-b} \cdot F}{m} = \frac{(10^{-pH_a} - 10^{-pH_b}) \cdot F}{m} \qquad (2)$$

The curve of 2 mM KNO_3 was arbitrarily fixed, so the surface charge at the lowest pH of this curve (pH=±3) was set equal to zero. For each of the other curves the surface charge at the pH, measured in the separate experiment, was taken as the sum of $\Delta\sigma$ from equation (2) and $\Delta\sigma$ from equation (1) at 2 mM KNO_3. The result will be referred to as the "(relative) surface charge".

In figures 7 and 8 the change in surface charge with pH for microcrystalline cellulose and cotton linters, respectively, is shown. The relative charge on the microcrystalline cellulose is −1 C/g. The absolute charge will be slightly higher, since at pH=4 part of the carboxylate groups is already dissociated. Compared to cellulose fibers, where at pH≈7 the charge varies from −3 C/g for bleached sulphate pulp to −10 C/g for unbleached sulphate pulp [5], the charge on MCC is low. Edelson and Hermans [23] performed potentiometric titrations of microcrystalline cellulose, or more correct, level-off DP cellulose, the same material we have used. They started their titrations at pH=2 and assumed that all proton-bearing groups were protonated. With a simple formula for the dissociation constant of a weak acid they obtained pK=4 for the acidic groups, which are probably carboxylate groups. The groups with pK=9.2 were not bound to cellulose, but were identified as ammonia, due to their sample preparation. If at pH=2 all carboxylate groups are protonated, the charge on the level-off DP cellulose amounts to −1.13 C/g. This is close to the surface charge we have found. The surface charge of cotton linters is smaller, approximately −0.6 C/g. Herrington and Midmore [5] found an absolute charge of −0.5 C/g from their potentiometric titrations and a point of zero charge at pH around 2. Both values agree well and it seems that our relative values of the surface charge are rather close to the absolute values. Their charge/pH isotherms show an increase in charge for pH>7, like ours, attributed either to swelling of the fiber in alkali solutions which opens up new acid groups, or to a second weak acid group. This second weak acid group could also be a carboxylate group, but one that is present at low pH as a lactone and opens up at high pH [4, 24].

The effect of the salt concentration on the shape of the titration curves, shows that the charged groups are close enough to interact. At high salt concentration, the charges of neighbouring groups are screened and protons are released more easily, i.e. at lower pH. At pH of about 7, all groups are dissociated, so the salt effect disappears. For pH's higher than 7, no salt effect is visible. This can be caused by the fact that the new dissociating groups are located in pores, where the electric field is screened by the counterions.

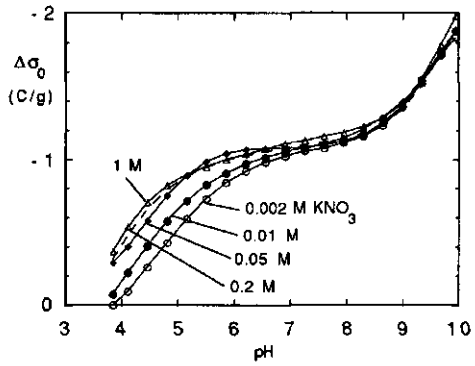

Figure 7. Charge/pH isotherm of (untreated) microcrystalline cellulose at various salt concentrations (indicted in graph).

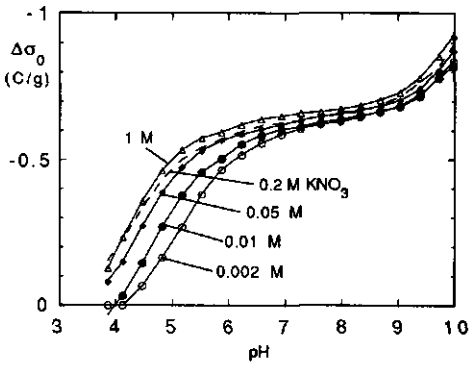

Figure 8. Charge/pH isotherm of cotton linters at various salt concentrations (indicated in graph).

3.1.7 Specific surface area of microcrystalline cellulose

The specific surface area is an ambiguous quantitity for porous substrates like cellulose fibers. When researchers discuss the specific surface area they sometimes refer to the surface without pores as *exterior* surface and to the surface including the pores as *interior* surface [25]. Since microcrystalline cellulose is level-off DP cellulose, the pore structure is probably preserved, so the available surface area can be different for small and large molecules. Therefore the measured specific surface area will depend on the applied method, and the size of the molecules used for it.

With N_2 adsorption the BET surface area of microcrystalline cellulose was found to be 1.1±0.3 m^2/g. Other investigators have also found such a small surface area: 2.5 m^2/g (BET, krypton adsorption, [26]) and 1.32 m^2/g (BET, argon adsorption, [27]). The reason is probably the same as for cellulose fibers, which generally also have a very small surface area when determined with gas adsorption, namely the collapse of the pores in the drying procedure. This collapse can be prevented using a special

drying technique, namely solvent-exchange [8, 9, 10] but, to the author's knowledge, for solvent-exchanged microcrystalline cellulose the BET surface area has not been reported in literature. Therefore, the BET surface area as we determined it, is not very useful for our adsorption experiments with cationic starch.

The specific surface area of microcrystalline cellulose measured in aqueous solution probably gives a more realistic value. The distribution of cations or anions in the diffuse double layer can be used to determine the specific surface area. Herrington and Midmore [28] for instance, used negative adsorption of chloride ions. Van der Toorn [29] investigated the adsorption of the organic cation paraquat (1,1-dimethyl-4,4-bipyridinium chloride) on microcrystalline cellulose and concluded that paraquat does not adsorb specifically, but stays in the diffuse double layer. By double layer calculations she estimated the specific surface area of microcrystalline cellulose to be 60 m^2/g. From the potentiometric titrations we know the charge on microcrystalline cellulose to be about -1 C/g at pH=7, so then the surface charge density at pH=7 is 0.017 C/m^2.

However, paraquat ions are very small and are probably able to enter all pores. From solute exclusion techniques, it is known that uncharged dextranes with molecular weight larger than 10,000, can not enter most pores, which means that the average pore size in swollen cellulose fibers is about 50 Å [30, 31]. To obtain more information on the available surface area for polyelectrolytes, the adsorption of polyDiMethylDiAllylAmmonium Chloride (DMDAAC, structure see figure 9) with two different molecular weights was measured (figure 10). Both DMDAAC-polymers were obtained from Allied Colloids, and their weight average molecular weights, as determined from size exclusion chromatography calibrated with monodisperse PEO polymers, were $3 \cdot 10^4$ and $1.1 \cdot 10^6$. They were quite heterodisperse, since the smallest polymer has $M_w/M_n=3.5$ and the largest $M_w/M_n=6$, also determined with size exclusion chromatography. Cleaned cellulose was used for the adsorption isotherms and the equilibration time was about 1 hour. Since no salt was added, the highly charged polymers will adsorb entirely by charge compensation, so we can determine the surface charge from the adsorbed amount [32]. In figure 10 we can see that the adsorbed amount for both polymers differs significantly. From the potentiometric titrations we know the charge on microcrystalline cellulose to be about -1 C/g at pH=7. The maximum adsorbed amount of the smallest polyDMDAAC, 0.75 g/g, corresponds to a charge of 0.4 C/g at pH=7, so the accessible charge for this molecule is 40% of the total charge. The largest polyDMDAAC is able to compensate

about 1/3 of this charge. This means that only 13% of all charges is accessible for the largest polymer and the same probably amounts to the accessible surface area, so that is about 6 m^2/g. It is to be expected that, as soon as molecules are excluded from the pores, the accessible surface area will stay the same, also for larger molecules. Experiments reported by Wågberg et al. [33] confirm this. Therefore we can conclude that, although cationic starch has a larger molecular weight than the largest polyDMDAAC, the available surface area will be approximately the same, namely 6 m^2/g.

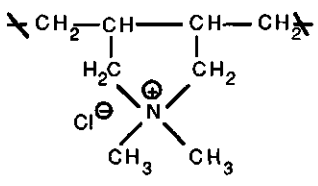

Figure 9. Structure of poly-DMDAAC

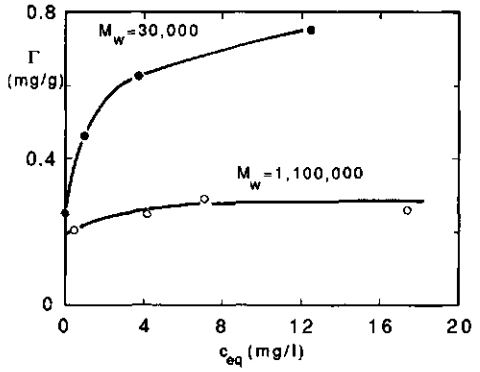

Figure 10. Adsorption of polyDMDAAC's with different molecular weights on cleaned microcrystalline cellulose, pH≈7, no salt added.

3.2 Cationic starch

3.2.1 Properties of native starch

Starch constitutes the major food reserve material of all the higher plants. It is laid down in seeds, roots and tubers in the form of particles that are insoluble in cold water, the so-called starch granules containing polymers of α-glucose. The monomer unit of starch differs from the cellulose monomer unit β-glucose in the position of the oxygen atom at C1 (figures 1 and 11). Starches can, in general, be separated into two chemically distinguishable entities: amylose, a mixture of essentially linear polymers of α(1,4)-glucose, and amylopectin, a mixture of highly branched polymers with α(1,4)-bonds in the linear parts and α(1,6)-bonds at the branching points [34]. Most starches contain 15-30% amylose, the exact amount depending on the botanical source. Potato starch contains 21% amylose and 79% amylopectin. The starch from waxy maize, a special corn variety, contains only amylopectin [35, 36].

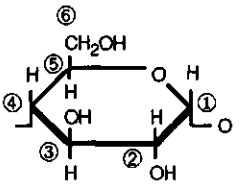

Figure 11. Structure of an α-glucose unit.

When starch granules are heated in boiling water ("cooking") they swell irreversibly, rupture and desintegrate, yielding a viscous dispersion of swollen granule fragments and dissolved molecules. In order to obtain molecularly dissolved starch, the temperature has to be high enough (at least 100°C) and the dispersion has to be stirred very well whilst cooking. The irreversible swelling is also called gelatinization. When starch solutions are allowed to stand, the phenomenon known as *retrogradation* can take place. This is manifested in the formation of a gel in concentrated solutions or a precipitate in dilute solutions. Amylose has the highest tendency to retrograde, amylopectin hardly retrogrades due to its branched structure.

Amylose has a molecular weight of the order of 10^5-10^6 [35, 36]. It contains a linear and a slightly branched fraction [34, 37]. The branched fraction can make up 30-70% of the total and contains branched molecules with 5-17 chains [38]. These few branches do not influence the hydrodynamic behaviour of amylose. Water is a solvent in which amylose behaves as a random coil, as is expected for a linear molecule. It is an expanded coil in a good solvent like dimethylsulphoxide or aqueous alkali. In the presence of a complexing agent (for instance I_2 or butanol) or in aqueous solution at pH 12 in the presence of 0.3 M KCl, amylose exists as a helix [34].

The molecular weight of amylopectin is of the order of 10^7 or 10^8 [35, 36], making it one of the largest of the natural polymers. Amylopectin contains some 4-5 per cent of α-1,6-branch points [34, 39]. In recent years much research has been devoted to the determination of the branched structure of amylopectin, especially with enzymatic methods. From this the general view has emerged that amylopectin has a cluster type structure [34, 39, 40] (figure 12). Two types of chains are involved: A-Chains, which are linked to the molecule only by the potentially reducing group, and B-chains, which are similarly linked, but in addition carry one or more A-chains. In most amylopectin samples there are somewhat more A-chains than B-chains, the ratios ranging from about 1:1

to 1.5:1. The exterior chain length, between a free end and a branching point, is usually 8 glucose units, and the interior chain length, between the branching points, ranges from 12-15 units in most samples [39]. The cluster type structure is in accordance with the fact that amylopectin has a relatively high viscosity as compared to glycogen, an α-1,4-polyglucan with about 10 per cent α-1,6-branch points, and an even higher molecular weight. Banks and Greenwood [34] compared a glycogen and an amylopectin with the same gyration radii and found that the molecular weight of the latter is a factor 6 smaller. Hence amylopectin has a more open molecular structure. This is also evident from the ability of amylopectin to swell in a good solvent, whereas glycogen hardly swells at all [34]. From NMR diffusion measurements, Callaghan et al. [41] concluded that in solution, wheat and potato amylopectin have the shape of an oblate ellipsoid (like a pancake). Such a shape for amylopectin was also suggested by Banks and Greenwood [34], based on the synthesis of amylopectin as a two-dimensional entity and its hydrodynamic behaviour.

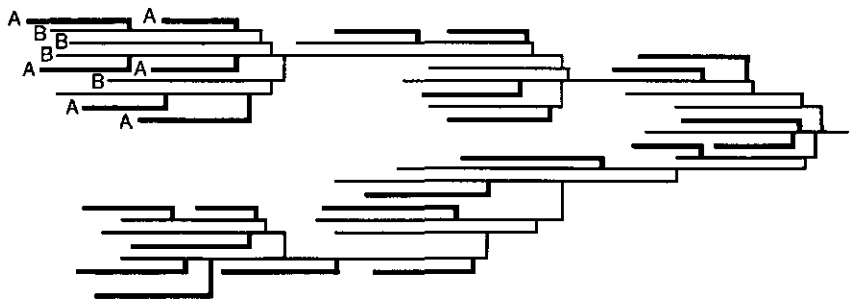

Figure 12. Cluster structure of amylopectin [34, 39, 40].

3.2.2 Starch derivatives

A large variety of starch ethers or esters can be prepared [42] for all kinds of purposes. Introduction of a few groups per 100 glucose units increases the solubility of starch and effectively suppresses the tendency of starch solutions to retrograde [36]. Cationic starches are used in the paper industry to improve dry strength and retention [43, 44]. Currently, tertiary aminoalkyl and quaternary ammonium starch ethers are commercially most significant. They are prepared by reaction between slightly swollen starch granules and reagents containing amino or ammonium groups at pH 11 to 12. Due to the limited accessibility of starch in the granules, their degree of substitution (DS) is usually below 0.05, which means that, at most, 5 out of 100 glucose units have a

Table 2. Distribution of groups over amylose and amylopectin in starch derivatives.

substitution with	DS_{starch}	$DS_{amylose}$	$DS_{amylopectin}$	DS_{am}/DS_{ap}
DEAE[1]	0.003	0.005	0.003	1.7
DEAE[1]	0.006	0.008	0.004	2.0
DEAE[1]	0.01	0.012	0.009	1.3
DEAE[1]	0.01	0.013	0.009	1.5
methyl[2]	0.006	0.007	0.004	1.8
methyl[2]	0.016	0.021	0.014	1.5
quaternary ammonium[3]	0.03	0.022	0.035	0.63

[1]Diethylaminoethyl ether groups, Steeneken [45]
[2]methyl ether groups, Steeneken et al. [46]
[3]2-hydroxy-3-trimethylammonium ethergroups, Salomonsson et al. [47]

cationic group; by definition the maximum DS is 3, since every glucose unit has three hydroxyl groups available for an ether or ester bond. The DS is determined by measuring the nitrogen content of the starch sample. The distribution of the cationic groups seems to be fairly homogeneous since for diethylaminoethyl (DEAE) starch no di- or tri-substituted residues were found. Most DEAE groups were located at the C-2 or C-6 carbon atoms in the glucose unit [44].

Since cationization takes place in the granule, the cationic groups are not necessarily equally distributed over amylose and amylopectin. Amylose is the main component of the amorphous parts of the granule, while amylopectin mainly constitutes the crystalline regions. The amorphous parts will probably react more easily so that amylose is preferentially substituted. In table 2 the results of investigations concerning the distribution of groups over amylose and amylopectin in potato starch are summarized. It seems that the reactivity of amylopectin increases with increasing DS.

3.2.3 Materials

Cationic potato starches with a degree of substitution of 0.017 ("Amylofax 00"), 0.035 ("Perfectamyl PW") and 0.047 ("Amylofax HS") were kindly provided by Avebe, Foxhol, the Netherlands. The cationic charge originates from quaternary ammonium groups (2-hydroxy,3-trimethylammonium-propyloxy starch).

Cationic waxy maize starch, "Resistamyl 132", was kindly provided by Zetmeelbedrijven "De Bijenkorf", Koog aan de Zaan, the Netherlands. It has a degree of substitution of 0.035 (nitrogen content (w/w) 0.31%).

The cationic groups are quaternary ammonium groups (2-hydroxy,3-trimethylammonium-propyloxy starch).

3.2.4 Phosphorus content

Potato starch contains phosphate ester groups which are chemically bound either to the C6-(2/3) or C3-(1/3) position of glucose units of the amylopectin molecules [48]. The monophosphate esters are evenly distributed over the B-chains of the amylopectin molecules [49]. Since a high pH is necessary for the cationization reaction and ester bonds can rupture at high pH, we wanted to know whether or not our cationic starches still contained phosphate groups. The phosphorus content of the three cationic potato starches was determined with ICP-AES (inductively coupled plasma atomic emission spectrometry). We did not determine the P-content of a solution of native potato starch because we expected its retrogradation to give rise to detection problems (a solution with gel-like particles can not be dispersed properly in air). The results are given in table 3. All three starches contained ±2 mmol P/mol glucose units, or 1 phosphate group per 500 glucose units, which is in good agreement with values of 1 phosphate ester per 100-400 glucose units reported in literature for native potato starch [36, 48]

The phosphate content was also determined in the dry material with a colorimetric method [50]. Its detection limit is a few nanomoles. As we can see in table 3 the values obtained with this method are in the same

Table 3. Phosphorus content of native potato starch and its cationic derivatives.

sample (1)	g/l	method (2)	mg P/l	mol P/g starch (x 10^5)	mmol P/mol glucose units
potato starch		col		2.27	3.7
amylofax 00		col		2.16	3.5
amylofax 00	1	ICP	0.42		2.3
amylofax 00	2	ICP	0.77		2.1
perfectamyl PW		col		1.69	2.7
perfectamyl PW	1	ICP	0.33		1.8
perfectamyl PW	2	ICP	0.68		1.8
amylofax HS		col		2.18	3.5
amylofax HS	1	ICP	0.37		2.0
amylofax HS	2	ICP	0.80		2.1

(1) potato starch is native starch. Amylofax 00, perfectamyl PW and amylofax HS are cationic potato starches with DS of respectively 0.017, 0.035, 0.047.
(2) ICP stands for Inductively Coupled Plasma Atomic Emission Spectrometry, col is the colorimetric phosphate determination according to [50].

order of magnitude, but about 1.6 times higher than those obtained with ICP-AES. The phosphate content of native starch is about the same as that of cationic starch, so it is hardly affected by the cationization. It should be noted that we do not know if the phosphorus is chemically bound.

The phosphorous content of cationic waxy maize solutions was determined with ICP-AES and no phosphorus could be detected. The P detection limit is 0.076 mg/l, which corresponds to 0.4 mmol P/mol glucose units or 4 phosphate groups per 10,000 glucose units for a starch solution of 1 g/l.

3.2.5 Preparation of starch solutions

Solutions of cationic potato starch were prepared according to a procedure recommended by Avebe. A solution of 50 g cationic starch in 0.5 l 0.01 M NaCl was cooked on a boiling water-bath for 30 min under vigorous mechanical stirring with a specially devised stirrer. The stirring speed was 600 rpm till gelatinization (2-3 min) and was then increased to 1100 rpm. According to Avebe, starch solutions prepared in this way are comparable to starch solutions cooked in a jet cooker at 120-130°C. The solution was diluted with water to 25 g/l.

Starch solutions are known to be subject to microbial degradation. The degree of degradation can be detected by measuring the viscosity of the starch solution (5 g/l, capillary viscosimeter), since the viscosity η of entangled polymers is very sensitive to changes in molecular mass ($\eta \approx M_W^{3.4}$ [51]). It was found that without measures, the viscosity of a Perfectamyl PW solution decreased to 50% of the original value in one week, which would imply that the average molecular weight decreased by 20%. Therefore it was considered necessary to develop a method for the conservation of starch solutions. Sterilization of the starch solutions (25 g/l, 2.5 mM NaCl), for about 30 min at 120°C, proved to be very satisfactory in this respect. The viscosity of sterilized cationic starch solutions only drops 7% in 3 months. This small decrease in viscosity is probably due to hydrolysis catalyzed by H^+-ions. Sterilization has the advantage that it prevents the use of a biocide, which would be an unwanted additional component in the system.

Cationic waxy maize starch solutions were prepared in the same way, except for the rate of stirring and the cooking time. After gelatinization the solution was vigorously stirred at 2000 rpm for 2 hours. It was diluted and sterilized as potato starch solutions. Even the high shear forces and long cooking time could not prevent part of a 1 g/l solution diluted from the 25 g/l stock solution, to end up at the bottom of the centrifuge tube after 10 min at 170*g*. The solution must have contained large fragments

of partly destroyed granules or amylopectin gel. This is very well possible, since Banks and Greenwood [34] reported that waxy maize is difficult to solubilize, although very susceptible to vigorous stirring. After 1 hour of centrifugation at 48,400*g*, a freshly prepared cationic waxy maize solution (long cooking time) of 2 g/l showed a small pellet. When the supernatant was centrifuged again for 10 min at 170*g*, no starch moved to the bottom. This is an indication that the sample contained undissolved granules. We also observed the following effect of time on cationic waxy maize solutions. Of a 1 g/l cationic amylopectin solution (0.1M NaCl) taken from a nine months old 25 g/l stock solution (stirred 30 min at 1100 rpm) about 20% was centrifuged off after 10 min at 6000 *g*, whereas only 9% was centrifuged off from a 1 g/l cationic waxy maize solution (0.1M) taken from a three weeks old stock solution prepared in precisely the same way. At first it seems unlikely that this would be due to retrogradation, since it is generally accepted that amylopectin solutions do not retrograde as easily as amylose solutions [36]. For example, Ring et al. [52] found retrogradation of solutions of waxy maize at 1°C for concentrations larger than 10%, whereas for smaller concentrations no retrogradation was found after a period of 6 weeks. It is also known that retrogradation is to a large extent prevented by derivatizing the starch with a small amount of ether or ester groups (two or three of such groups per 100 glucose units is sufficient [36]). On the other hand, nine months is a very long time, so we think that the aging effect is, in fact, retrogradation.

3.2.6 Sedimentation coefficients

Sedimentation coefficients of cationic amylose and amylopectin were determined by centrifugation of a solution of 5g/l perfectamyl, 0.1 M NaCl, in a MSE Centriscan analytical ultracentrifuge. During centrifugation the distribution of the macromolecules in the cell changes. This can be monitored during the run, either by means of absorption of UV- or visible light, or with a Schlieren-optical system. For amylopectin we used absorbance at λ=305 nm, taking scans every 2 min while spinning at 15,000 rpm. For amylose we employed the Schlieren optical system, and we took scans at 5 min intervals, using a rotation speed of 45,000 rpm. The sedimentation coefficients $S_{t,s}$, obtained at temperature t and with a certain solvent s (0.1 M NaCl in our case) are obtained by plotting ln r (r is the distance between the sedimenting molecules and the center of the rotor) against elapsed time (s) and determining the slope $S\omega^2$, where ω is the angular velocity [53]. $S_{t,s}$ can be converted to the corresponding value at zero concentration in water at 20°C, $S_{20,w}$:

$$S_{20,w} = S_{t,s}\left(\frac{\eta_{t,s}}{\eta_{20,w}}\right)\left(\frac{1-\bar{v}\rho_{20,w}}{1-\bar{v}\rho_{t,s}}\right) \qquad (3)$$

where η is the viscosity of the solution indicated by the subscript, $\bar{v}$ is the partial specific volume and ρ is the density. The viscosity $\eta_{t,s}$ of 5 g/l perfectamyl in 0.1 M NaCl at t=25°C (we supposed that it was the same for 20°C) was experimentally determined (see 3.2.7, capillary with ø 0.88 mm) at $1.43 \cdot \eta_W$. For $\bar{v}$ we used 0.62 cm^3g^{-1}, a value reported by Banks and Greenwood [35]. We determined $\rho_{t,s}$ to be 1.0038 g/ml (see 3.2.8) at t=20°C. For amylose we obtained $S_{20,w}$=5.8 S[1)] and for amylopectin $S_{20,w}$=199-220 S which agree well with values in literature. Banks and Greenwood [35] reported for potato amylopectin in 0.2 M NaCl, S_0=255 S, corresponding to a molecular weight of $65 \cdot 10^6$, obtained by dynamic light scattering, and for potato amylose in 0.33 M KCl [54], S_0=4.55-16.3 S, corresponding to $M_w=0.16 \cdot 10^6$-$2.29 \cdot 10^6$. The sedimentation coefficient of amylopectin samples is not very sensitive to differences in high molecular weights, as is illustrated by a tapioca amylopectin with $M_w=450 \cdot 10^6$ for which in 0.2 M NaCl S_0=270 S was found [35]. Banks and Greenwood [35] attribute this insensitivity to heterodispersity of their amylopectin samples. S_0 was obtained by Banks and Greenwood by extrapolation to zero concentration of sedimentation coefficients measured at different concentrations of starch, so it is not exactly the same as our $S_{20,w}$. If we suppose S_0 and $S_{20,w}$ to be essentially the same, we can estimate the molecular weights of our amylose and amylopectin to be $3.5 \cdot 10^5$, and something between $5 \cdot 10^7$ and $5 \cdot 10^8$ respectively.

After fractionation of a perfectamyl solution by centrifugation (see 3.2.10) we determined the sedimentation coefficient of the amylose fraction in another way. We added some iodine solution [55] in order to obtain the blue amylose-iodine complex, which can be detected at λ=600 nm ($A_{600} \approx 0.5$, [NaCl]≈0.01 M). For this complex we found $S_{20,w}$=10.4 S. It is not clear whether the sedimentation coefficient of amylose is higher because we are dealing with the iodine complex, or because we could now detect a fraction of amylose with a larger molecular weight. It was impossible to determine the sedimentation coefficient of the pink amylopectin-iodine complex in the same way because it was centrifuged off immediately.

The sedimentation coefficient $S_{20,w}$ of cationic waxy maize was determined in the same way as that of amylopectin from cationic potato

[1)] S: Svedberg, 10^{-13} s.

starch, and found to be 152.7 S. This is in the same range as the sedimentation coefficient of amylopectin from cationic potato starch. We can estimate from [35] the molecular weight of the waxy maize amylopectin to be somewhat smaller than that of potato amylopectin, i.e. between $1 \cdot 10^7$ and $6.5 \cdot 10^7$. Our sedimentation coefficient is larger than the value reported by Banks and Greenwood [35]. They found S_0=55 S for a waxy maize solution which had been subjected to shear at high concentration (~15%). Although our waxy maize starch has been subjected to considerable shear during the preparation of the solution (30 min at 1100 rpm, as described in 3.2.5), the sedimentation coefficient does not seem to be affected. Probably our shear forces were weaker.

3.2.7 Changes of molecular volume with salt concentration measured by viscosity and dynamic light scattering

The viscosity of starch solutions was measured with an automatic capillary viscosimeter (Fica viscomatic MS, type 53 000). We measured the time needed for a fixed volume of 0.5 g/l perfectamyl PW and cationic waxy maize solutions to flow through a capillary with ø 0.5 mm as function of NaCl concentration at 25°C. We also measured the dispension time for water. In figure 13 the specific viscosity over the concentration, η_{sp}/c, is plotted as a function of the NaCl concentration. It is clear that increasing salt concentration leads to shrinking of the cationic starch molecules due to screening of repulsion between the charged groups. The shrinkage of cationic amylopectin from waxy maize is comparable to that of cationic

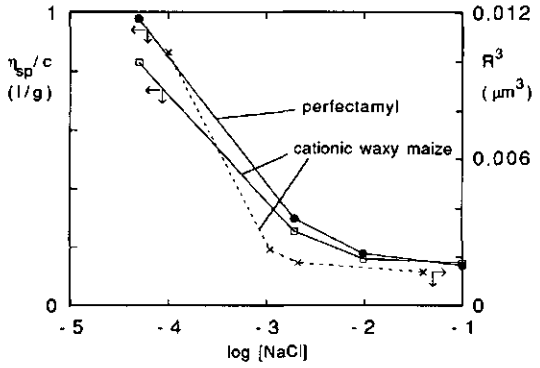

Figure 13. The specific viscosity, η_{sp}/c, of cationic potato starch (perfectamyl) and cationic waxy maize solutions, as a function of the salt concentration (left hand axis) at t=25°C. In the same graph the third power of the hydrodynamic radius R of cationic waxy maize solutions, as measured with dynamic light scattering, is plotted against the salt concentration (right hand axis).

potato starch with the same DS. This is understandable since the viscous behaviour of potato starch will be dominated by amylopectin (80%).

With a dynamic light scattering experiment (angle: 90°) we also obtained an impression of the change in hydrodynamic radius of the cationic (waxy maize) amylopectin molecules with increasing salt concentration. We can compare the results of dynamic light scattering with the viscosity measurements if we assume that the viscosity of the starch solutions is related to the molecular volume, and that, as a first approximation, the shape of these molecules is spherical. In figure 13 the third power of the hydrodynamic radius R is also plotted against the salt concentration. The dynamic light scattering experiment shows the same trend as the viscosity measurements, namely that the largest amount of shrinking occurs if the salt concentration is increased from almost zero to 2 mM.

3.2.8 Density of starch solutions

Due to the high viscosity of the starch solutions it was not possible to use pipettes for the dilution of starch solutions. Therefore, the amount of the solution needed was always weighted. The density of perfectamyl PW solutions was determined with a pyknometer at 20°C. The results are given in table 4.

Table 4. Density of cationic potato starch solutions

[perfectamyl] (g/l)	[NaCl] (M)	ρ (g/ml)
0	0.002	0.9982
1	0.002	0.9984
10	0.002	1.0012
25	0.002	1.0064
0	0.1	1.0024
1	0.1	1.0024
10	0.1	1.0055

We assumed the density to be linear with concentrations between 0 and 2.5 g/l. For different NaCl concentrations we added the density difference between a 2 mM NaCl solution and the required NaCl solution [56] to the density of the starch solution in 2 mM NaCl.

The density of cationic waxy maize solutions was taken to be the same as the density of perfectamyl PW solutions.

3.2.9 Fractionation of cationic potato starch by ultracentrifugation

The large difference in molecular weight can be used to separate amylose and amylopectin. We centrifugated 5 g/l solutions of perfectamyl in 0.1 M NaCl for 1 hour at 120,000*g*, and obtained a sharp boundary separating an opaque viscous fraction ("pellet") and a clear supernatant. Both the supernatant and the "pellet" (diluted with 0.1 M NaCl to fill the centrifuge tube again) were centrifugated once more. The amylose/amylopectine ratio was determined according to [57], using their extinction coefficients, but with the iodine solution as used in [55]. The amylose fractions were found to be 0.675 for the supernatant and 0.04 for the "pellet", which means that solutions with respectively 67.5% cationic amylose and with 96% cationic amylopectin were obtained. The carbohydrate concentration of the solutions was determined according to [14] (see also 3.4.1).

The NaCl-concentration in amylose-rich, amylopectin-rich and perfectamyl solutions was 0.1 M and they were dialysed for two days until the specific conductivity of the solutions was 40-60 μS/cm. Before using, the dialysis tubing (Thomas Tubing, cat. no. 3787-D22, $M_{w,cut\text{-}off}$=12,000) was boiled respectively in water with EDTA and in water only, and afterwards thoroughly rinsed with water.

3.3 Determination of starch concentrations

3.3.1 Carbohydrate determination according to Dubois et al.

The sulphuric acid-phenol (SP) method [14] is a general method for the determination of carbohydrates, since the glucose-unit provides the colour. With the SP-method the total amount of starch, that is amylose and amylopectin, can be determined. Ferric ions interfere with the color reaction [58], so the sulphuric acid should be free of these ions. Other carbohydrates present in solution (cellulose, hemicelluloses) have to be removed carefully. Cellulose was removed by centrifugation and starch was determined in the supernatant (see also 3.5.1). Since some hemicellulose was left in the supernatant (see 3.1.5) the absorbances were corrected for a cellulose blank, i.e. a suspension of cellulose in the same medium as used for the adsorption measurements without starch, and treated in the same way as the samples with starch. For cellulose cleaned as described in 3.1.5, usually A_{490}≈0.1.

We added 125 μl of an 80% (w/w) phenol in water solution to 2 ml starch solution, mixed and added 5 ml of concentrated (95-98%) sulphuric acid. Automatic pipettes were used. The tubes were allowed to stand for 10 minutes, the solution was mixed, and was then placed in a

water bath at a temperature between 25 to 30°C for 10 to 20 min. The absorbance at 490 nm was about 1 for a solution of 50 mg/l starch. We found that the absorbance of the same carbohydrate solution was less if 1 ml of 5% phenol in water solution is used instead of 80% phenol, as is also suggested by Dubois et al. An explanation might be that the starch was not completely destroyed, because temperature will become somewhat lower in the larger total volume. We also noticed that the intensity of the orange colour was different if the starch solution was allowed to stand some time after addition of phenol. Therefore, we always added sulphuric acid immediately after the addition of phenol before continuing with the next sample.

3.3.2 Starch determination with iodine

In 1814, only three years after the discovery of iodine, the reaction of this element with starch in aqueous solution to yield a brilliant blue colour, was noted. More than a century later it became clear that this blue colour originates from iodine occupying the cavity of a helical amylose molecule [34, 59]. The most important applications of this colour reaction are the determination of starch and the distinction between amylose and amylopectin, based on their different iodine-binding capacities. Under the right conditions amylose binds some 20 per cent of its own weight of iodine whilst amylopectin binds none (the circumstances under which amylopectin binds iodine will be discussed below).

In a starch determination with iodine, the colour depends on pH, temperature, degree of polymerization (DP), ratio of amylose and amylopectin, concentration of I_2, and concentration of KI [34, 59]. At pH>8 and temperature>30°C the intensity of the colour becomes less and disappears at much higher pH and temperature [59]. The minimal DP of a linear α(1,4)-polyglucan which gives a coloured complex with iodine, is 12, and the complex displays a pale shade of pink with a wavelength of maximum absorbance λ_{max} at about 500 nm [60, 61]. Between DP=12 and DP=100, the colour of the polyglucan-iodine complex changes from pink to blue and λ_{max} increases from 500 to 610 nm [35, 60, 61]. For DP>250, λ_{max}=642 nm [34], so this is also the wavelength were the absorbance of the amylose-iodine complex is maximal. The colour of the amylopectin-iodine complex is pink (λ_{max} is usually about 550 nm) instead of blue, since the branches of the amylopectin molecule are shorter than the 50 glucose units necessary to obtain the blue colour [60, 61]. Based on the iodine-binding capacity of amylopectin, Banks and Greenwood [34] concluded that the length of the external parts of amylopectin is less than

about 15 glucose units, whereas Thorn [60, 61] found from the colour of the iodine complex, that the main chain, which is the part of the chain left after enzymatic debranching, consists of about 40 glucose units.

The amount of iodine bound by amylose and amylopectin depends on the concentration of I_2 and KI in the solution. KI must be present in solution for the formation of the starch-iodine complex. The absorbance at λ_{max} is linear with the amount of bound iodine and at a concentration of 0.01 M KI (1660 mg/l), the largest amount of iodine is bound by amylose [34]. Amylopectin-iodine complexes are only formed to some extent if a large excess of I_2 is present [34]. This means that, if the iodine

Table 5. Sensitivity of the TAPPI, Williams and Hovenkamp-Hermelink methods for amylose and amylopectin at different wavelengths in water

Method according to Williams et al. [55]: $[I_2]$=20 mg/l and [KI]=200 mg/l				
λ (nm)	ε_{wap}	ε_{st}	ε_{am}	$\varepsilon_{am}/\varepsilon_{ap}$
550	4.83	7.88	19.35	4.01
618	3.09	9.38	33.04	10.69
625	2.88	9.26	33.22	11.5
Method according to TAPPI [62]: $[I_2]$=250 mg/l and [KI]=750 mg/l				
λ (nm)	ε_{wap}	ε_{st}	ε_{am}	$\varepsilon_{am}/\varepsilon_{ap}$
550	9.16	12.37	24.44	2.67
580	7.96	13.42	33.94	4.26
618	5.98	12.82	38.54	6.44
625	5.63	12.56	38.67	6.87
Method according to Hovenkamp-Hermelink et al. [57]: $[I_2]$=61.7 mg/l and [KI]=123.5 mg/l				
λ (nm)	ε_{ap}	ε_{st}	ε_{am}	$\varepsilon_{am}/\varepsilon_{ap}$
550	5.1	7.28	15.5	3.03
618	3.5	7.68	23.4	6.69

ε =extinction coefficient in $ml \cdot mg^{-1} \cdot cm^{-1}$
wap =cationic waxy amylopectin from waxy maize (Resistamyl)
st =cationic potato starch (Perfectamyl PW)
am =cationic amylose from cationic potato starch (Perfectamyl PW)
It is assumed that $\varepsilon_{st}=0.21 \cdot \varepsilon_{am}+0.79 \cdot \varepsilon_{ap}$ for all wavelengths.

concentration is not too high, in a mixture of amylose and amylopectin the former binds the largest amount of iodine and therefore contributes most to the colour.

In table 5 we compare three different iodine determinations of starch, namely the methods according to Williams et al. [55], TAPPI [62] and Hovenkamp-Hermelink et al. [57]. Williams et al. added 1 ml of a solution containing 2 g I_2 + 20 g KI per litre water, to 100 ml starch solution ($[I_2]$=20 mg/l and [KI]=200 mg/l). According to TAPPI, 5 ml of a solution with 5 g I_2 + 7.5 g KI per litre water, must be added to 100 ml starch solution ($[I_2]$=250 mg/l and [KI]=750 mg/l), whereas Hovenkamp-Hermelink et al. added "to 4 ml of starch solution 5 ml of a diluted (1:2, v/v) Lugol's solution (Merck, 2 g KI + 1 g I_2 in 300 ml H_2O)" ($[I_2]$=61.7 mg/l and [KI]=123.5 mg/l). The extinction coefficients for cationic waxy maize (Resistamyl) solutions and cationic potato starch (perfectamyl PW) solutions were determined in deionized water for the Williams and the TAPPI method, the extinction coefficients obtained in the Hovenkamp-Hermelink method were taken from their paper [57].

These three methods differ in their final iodine and iodide concentrations because they serve different purposes. The Williams method is designed to determine the amylose content of a starch sample, therefore the concentration of iodine is low and the absorbance is measured at 625 nm. From table 5 it is clear that from the three methods, the difference between the absorbance of amylose and amylopectin is indeed the largest in the Williams method. The purpose of Hovenkamp-Hermelink et al. is also to determine the amylose content of a starch sample, but they use the ratio R of the absorbance at 618 nm, to that at 550 nm. Assuming additivity of absorbance values, the fraction of amylose P can be calculated from the ratio R of the absorbancies at 618 and 550 nm according to:

$$P = \frac{(\varepsilon_{ap,618} - \varepsilon_{am,550} \cdot R)}{((\varepsilon_{am,550} - \varepsilon_{ap,550})R - \varepsilon_{am,618} + \varepsilon_{ap,618})} \qquad (4)$$

were ε is the extinction coefficient at the wavelength in the subscript, *am* denotes amylose and *ap* amylopectin. The TAPPI-method on the other hand, is meant to determine starch as sensitive as possible. Since amylopectin is the main constituent of starch, about 80%, a large amount of iodine is added to improve the absorbance of amylopectin. Moreover, in order to make the contribution of amylose and amylopectin to the absorbance as large as possible, it has to be measured at 580 nm. From table 5 it can be seen that indeed at this wavelength the absorbance of starch is largest.

In figure 14 the spectra for the iodine complexes of cationic waxy maize and cationic potato starch (perfectamyl), obtained by the TAPPI and the Williams method, are shown. From the higher value of λ_{max} for cationic potato starch in the Williams method in comparison to that in the TAPPI method, it is clear that the former is more sensitive for amylose. The latter has a higher sensitivity for amylopectin, as can be seen from the relatively higher absorbance at about 550 nm. The shape of the spectra for cationic waxy maize is almost the same for both methods, although the TAPPI method is obviously much more sensitive for amylopectin than the Williams method.

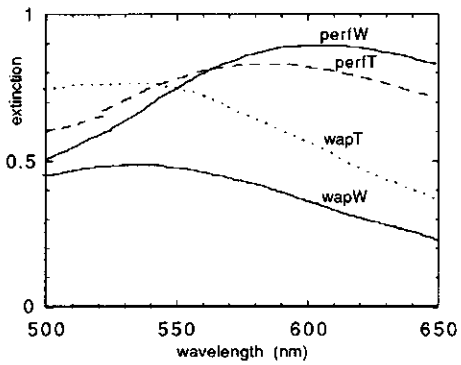

Figure 14. The spectra of the iodine complexes of cationic potato starch (perfectamyl, abbreviated as "perf") and cationic amylopectin, from waxy maize, (abbreviated as "wap") obtained by the Williams ("W") and the TAPPI ("T") method. The concentrations of the four solutions were: 100 mg/l for perfW and wapW, 60 mg/l for perfT and 80 mg/l for wapT.

We used the Hovenkamp-Hermelink method, including their values for the extinction coefficients of amylose and amylopectin, to estimate the amylose content in the samples obtained by ultracentrifugation, but with the same iodine solution as in the Williams method. From table 5 it clear that this is not correct, which we did not know at that time. We also found that the ratio R depends slightly on the concentrations of iodine and iodide, since A_{618}/A_{550} for cationic amylopectin is 0.65 in the TAPPI determination and 0.66 in the Williams method, whereas this ratio for cationic potato starch is 1.03 and 1.19 respectively. Hovenkamp-Hermelink et al. give R=0.69 for amylopectin only, and R=1.04 for starch with 21% amylose, the amylose content of potato starch. Nevertheless, we obtained a good indication of the amylose content of our samples.

The Williams method was used to determine cationic potato starch, because we wanted to distinguish between amylose and amylopectin. The

way we calculated the adsorption isotherms of amylose and amylopectin is described in 3.5.3. We noticed that if the NaCl concentration in the starch-iodine solutions was larger than 0.01 M, flocs developed, especially after a longer period of time, which in turn disturbed the absorbance measurements. Therefore, we measured the absorbance of starch-iodine solutions as quickly as possible and kept the salt concentration as low as possible. From table 6 it can be seen that the NaCl concentration also affects the extinction coefficients of amylose and amylopectin. In the determination of the equilibrium concentration of starch this was taken into account by measuring a calibration line at the salt concentration of the experiment.

Table 6. Effect of NaCl-concentration on the extinction coefficients of amylose and amylopectin at 550 and 625 nm in the Williams method

λ=550 nm [NaCl] (M)	ε_{wap}	ε_{st}	ε_{am}	$\varepsilon_{am}/\varepsilon_{ap}$
0	4.83	7.88	19.35	4.01
0.01	4.71	9.04	25.35	5.39
0.1	4.35	8.94	26.18	6.02
λ=625 nm [NaCl] (M)	ε_{wap}	ε_{st}	ε_{am}	$\varepsilon_{am}/\varepsilon_{ap}$
0	2.88	9.26	33.22	11.5
0.01	2.85	9.94	36.6	12.83
0.1	2.62	9.36	34.73	13.26

ε =extinctioncoefficient in $ml \cdot mg^{-1} \cdot cm^{-1}$
wap =cationic waxy amylopectin from waxy maize (Resistamyl)
st =cationic potato starch (Perfectamyl PW)
am =cationic amylose from cationic potato starch (Perfectamyl PW)
ap =amylopectin
It is assumed that $\varepsilon_{st}=0.21 \cdot \varepsilon_{am}+0.79 \cdot \varepsilon_{ap}$ for all wavelengths.

We used the TAPPI method to determine the waxy maize concentration, measuring the absorbance at 550 nm. In adsorption measurements identical equilibrium concentrations were found if waxy maize was determined with either sulphuric acid and phenol or with the TAPPI method.

3.4 Adsorption measurements

3.4.1 Adsorption isotherms

A volume V of a starch solution of known concentration (c_0), diluted from a sterile stock solution, was added to m grams of microcrystalline cellulose and shaken in an orbital shaker at 20°C. Equilibrium was established overnight, so during about 15 hours (see also below). After 10 min of centrifugation at 6000*g* in a swing-out rotor, the equilibrium concentration in the supernatant, c_e, was determined. For every adsorption experiment calibration lines were measured. The adsorbed amount Γ was calculated as:

$$\Gamma = \frac{(c_0 - c_e) \cdot V}{m} \qquad (5)$$

In experiments where the salt concentration was varied, the pH was not preset, otherwise it was estimated from the titration curves how much acid or base had to be added in order to obtain a certain pH. The pH was always measured after establishment of the equilibrium.

Although in all experiments the samples were equilibrated for one night, the adsorption of cationic waxy maize was once measured as function of time. We found that after five minutes 83% of the maximum (overnight) adsorbed amount was adsorbed and after one hour this value was completely reached. This is in agreement with the findings of other authors for adsorption of polyelectrolytes [63, 64, 65] and for the adsorption of cationic starch on cellulose [66, 67, 68, 69, 70].

The adsorption of cationic potato starch and cationic waxy maize was

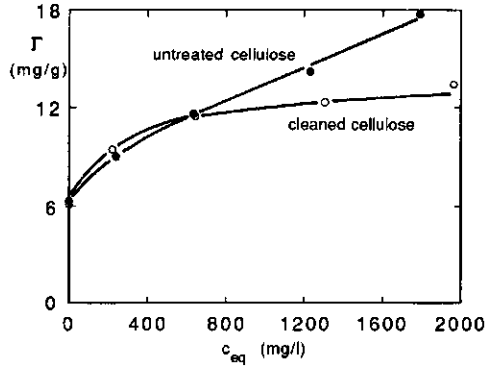

Figure 15. The total adsorbed amount of cationic potato starch (perfectamyl) on untreated and cleaned microcrystalline cellulose as a function of the equilibrium concentration of total carbohydrate, pH=6, 2mM NaCl.

hardly affected by the cleaning procedure for the microcrystalline cellulose. The adsorbed amounts on cleaned and untreated microcrystalline cellulose under the same circumstances were almost identical for $c_{eq} \leq 800$ mg/l (figure 15). For higher equilibrium concentrations the adsorbed amount on the untreated cellulose seems larger, which may (partly) be due to the experimental error.

3.4.2 Measurement of adsorption plateau values

From the adsorption isotherms, the plateau values were determined as were the starch concentrations necessary to reach them. For the assessment of the influence of [NaCl] on the plateau value of perfectamyl PW, the initial concentrations were 2.5 g/l. In the same experiment with cationic waxy maize these concentrations were 1 g/l, except for the [NaCl]>0.02 M, where the initial concentrations were 0.6 g/l.

As has already been mentioned in 3.2.5, centrifugation of a cationic waxy maize starch solution for 10 min at 6000*g* leads to a decrease of the concentration in the supernatant. We therefore centrifuged the starch solution of 2 g/l, from which all other solutions were diluted in one experiment, before the experiment for 10 min at 6000*g* and corrected for the waxy maize which was centrifuged off, by comparing the extinctions of the uncentrifuged and centrifuged solutions. After determination of the equilibrium concentration, starch solutions of the same concentrations and the same [NaCl] were centrifuged for 10 min at 6000*g* and corrected for the waxy maize centrifuged off in the same way. The amount of waxy maize that was centrifuged off depended on the starch concentration and [NaCl]. The lower the starch concentration and the higher the salt concentration, the more starch was centrifuged off.

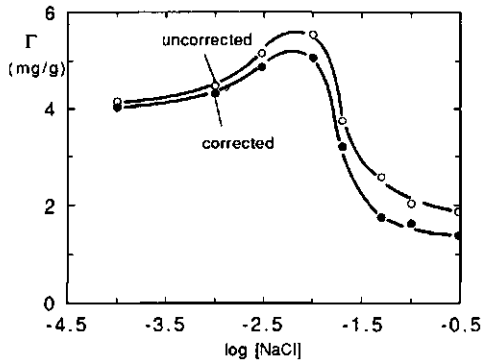

Figure 16. Effect of the corrections (described in the text) on the adsorption of cationic waxy maize on cleaned microcrystalline cellulose.

The first can be understood from the concentration dependence of the sedimentation coefficient, at low amylopectin concentration the sedimentation coefficient is highest [35], and the second can be understood from the screening of the repulsion between the cationic groups. Corrections ranged from 0-4%. In figure 16 an example of the effect of the corrections on the adsorptions is shown.

3.4.3 Calculation of the adsorption isotherms of amylose and amylopectin.

For adsorption measurements of cationic potato starch, the equilibrium concentration of all samples was determined with sulphuric acid and phenol (SP) [14], and the I_2-method according to Williams et al. [55]. The amylose concentration, c_{am}, and the amylopectin concentration, c_{ap}, (concentration in mg/l) were calculated from the absorbance A_{SP}, measured with the SP-method, the absorbance A_I, measured with the I_2-method, and the extinction coefficients, ε_{SP} and ε_I ($l \cdot mg^{-1} \cdot cm^{-1}$), by solving two equations with two unknowns:

$$\varepsilon_{I,am} \cdot c_{am} + \varepsilon_{I,ap} \cdot c_{ap} = A_I \quad (6)$$

$$\varepsilon_{SP,am} \cdot c_{am} + \varepsilon_{SP,ap} \cdot c_{ap} = A_{SP} \quad (7)$$

The following assumptions were made:

1. for the SP-method: $\varepsilon_{SP,starch} = \varepsilon_{SP,am} = \varepsilon_{SP,ap}$
2. for the I_2-method: $\varepsilon_{I,starch} = 0.21 \cdot \varepsilon_{I,am} + 0.79 \cdot \varepsilon_{I,ap}$
3. $\varepsilon_{I,am} = 11.5 \cdot \varepsilon_{I,ap}$

Since the SP-method is suitable for methyl derivatives of carbohydrates [14], assumption 1 will also be true for cationic starch. So from the SP-method we obtained the total carbohydrate concentration. In 2 we assumed that potato starch contains 21% amylose [36] and that the extinction coefficient of starch is a linear combination of those of amylose and amylopectin. The trends in the adsorption isotherms will not change if potato starch contains a little more (23%) or a little less (19%) amylose [71, 72]. From the experiments of Williams et al. [55] and Hovenkamp-Hermelink et al. [57] it appears that it is justified equating the weighted sum of absorbance of amylose and amylopectin with that of a mixture of these components. The extinction coefficient of starch is obtained from a calibration line. Assumption 3 follows from our measurements of the extinction coefficients of amylose and amylopectin given in table 5 and 6. We supposed that the extinction coefficient of amylopectin from potato starch is the same as that of amylopectin from waxy maize. Although the ratio of the extinction coefficients depends somewhat on the NaCl concentration, we used the same ratio for all adsorption isotherms irrespective of the salt concentration. The extinction coefficients we

obtained for (cationic) amylose ranged from 31.01 to 35.15 ml/mg·cm, and for (cationic) amylopectin from 2.7 to 3.06 ml/mg·cm. Williams et al. found about the same extinction coefficient for amylopectin (3.24 ml/mg·cm), but a higher extinction coefficient for amylose, namely 54.4 ml/mg·cm. The reason for this difference might be that the cationic groups in cationic amylose disturb the full development of the iodine-amylose complex. We did not observe significant differences between the extinction coefficients for cationic amylose with different DS.

3.5 Acknowledgements

Many people assisted in the characterization of the celluloses and the starches. I would like to thank: Hans van der Vis, Department of Food Chemistry for determining the monosaccharide content of microcrystalline cellulose and hemicellulose, Gerty Gielen and Bert van der Wal for their determination of the phosphorus content of the starches, Adri Westphal, Department of Biochemistry, for determining the sedimentation coefficients, Lars Wågberg and Inger Eriksson, SCA Research Sundsvall Sweden for the electron micrographs of solvent exchanged cellulose, Anton Korteweg for the BET-analysis and the determination of the density of starch solutions, Nynke Hoogeveen for the dynamic light scattering experiments and Lars Ödberg, Gunborg Glad-Normark and Agne Swerin, STFI Stockholm Sweden, for the adsorption isotherms of DMDAAC.

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4. ADSORPTION OF CATIONIC AMYLOPECTIN ON MICROCRYSTALLINE CELLULOSE

4.1 Introduction

A number of studies on the retention of cationic starch by cellulose and the effect of cationic starch on paper quality have been published [1-17]. Since in papermaking a small amount of cationic starch is added to the cellulose, usually 0.5-2% relative to the dry fiber weight, it is important to know which part of this amount is *retained*, and therefore most of the aforementioned papers deal with starch retention. Only some of these [8, 9, 10, 12, 13, 16, 17] have varied the amount of cationic starch added, or measured adsorption isotherms. Neither is it always clear what kind of cationic starch was used. The botanical source has not been specified although the performance of, e.g. corn starch and potato starch, is known to be rather different; for instance Vander Burgh [6] claims that cationic potato starch is twice as effective as cationic corn starch in a furnish[1] containing alum[2] and rosin size[3]. The nature of the cationic groups (tertiary amino groups or quaternary ammonium groups) is important for the influence of pH on the adsorption. The effect of this nature is clearly illustrated by Stoutjesdijk and Smit [7] by measuring the ζ-potential of cationic starch as a function of the pH. The charge of a cationic starch with tertiary amino groups decreases steeply between pH=3 and pH=5, and finally becomes zero at pH≈9.5, whereas the charge of a quaternary ammonium starch hardly changes between pH=3 and pH=9.

Marton and Marton [8] investigated the influence of the charge of cellulose fibers on the adsorption of a quaternary cationic potato starch. They found that on pulp with additional carboxylate groups more cationic starch was adsorbed than on virgin fibers, whereas on pulp with positive groups less cationic starch was adsorbed. They concluded that charge interactions are important driving forces for the adsorption of cationic starch on cellulose. Such a mechanism was vaguely suggested by Moeller [18] and Hernandez [5], but it is remarkable that for synthetic cationic polyelectrolytes charge interactions were already accepted much earlier as the driving forces for adsorption on cellulose [19].

The conclusion by Marton and Marton is further supported by the effect of the pH on the adsorption. Hernády and Völgy [9], Harvey [13] and Roberts et al. [15] found that the adsorption of cationic starch

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[1] furnish: the mixture of pulps and other materials (for instance, fillers and additives) before treatment, to make a particular paper.
[2] alum: papermaker's alum is a mixture of aluminium sulphate hydrates.
[3] rosin size: a rosin soap, which, with the added alum, gives the resulting paper a degree of water resistance.

increases with increasing pH, that is, with increasing dissociation of the carboxylate groups and therefore increasing charge on cellulose. Tanaka et al. [11] showed that the retention for cationic starches with secondary or tertiary aminogroups has a maximum as a function of the pH. The optimum pH for starch with secondary aminogroups is 9 and for tertiary aminogroups 11.5.

Hernády and Völgy also showed that if the pH is set with alum, the retention has a maximum at pH=6 [9]. Others [2, 5, 8, 18, 20] also investigated the effect of alum on the retention of cationic starch. Usually the effect is negative [5, 8, 18, 20], but sometimes the retention of cationic starch is increased [2]. Although the effect of alum is not well understood, it is clear that its influence depends on pH, since the formation of cationic aluminium hydroxide complexes is pH dependent [21, 22] and also on the alum concentration [20]. Only if phosphate groups are present, the performance of cationic starch is better in the presence of alum [13].

Marton [12] investigated the influence of the specific surface area and found that more cationic starch is adsorbed on fines, since fines have a larger specific surface area than fibers. The increased adsorption of cationic starch on fibers after beating [2, 9, 18] is probably caused by the increased amount of fines. However, fines do not only have a larger specific surface area, they also have a higher charge density [23].

The influence of temperature (0-60°C) on the adsorption of cationic potato starch on several types of cellulose fibers was investigated by Nedelcheva and Stoilkov [10]. Adsorption increased with temperature, which was explained by the existence of starch aggregates that disintegrate at higher temperatures. Separate molecules would adsorb better.

None of the studies took into account that also cationic starch is a mixture of amylose and amylopectin, although it is well known that native amylose is preferentially adsorbed on cellulose [24]. Some investigators have shown that if native amylose and amylopectin adsorb on cellulose separately, the adsorbed amount of amylose is higher [25, 26]. Van de Steeg et al. [17] demonstrated that from cationic potato starch solutions, cationic amylose is also preferentially adsorbed on microcrystalline cellulose.

In this paper the adsorption of cationic amylopectin was investigated as a first step in the fundamental understanding of cationic starch (a binary mixture) adsorption. Amylopectin was obtained from waxy maize, a genotype of maize containing amylopectin only. The effects of cellulose concentration, nature and concentration of salt, and pH on the adsorption

are studied. Microcrystalline cellulose was used as a model for cellulose fibers. We will first give the results and finally compare these with predictions of a recent theory on polyelectrolyte adsorption [27] (see also chapter 2).

4.2 Experimental

As described in chapter 3.

4.3 Results and discussion

4.3.1 Adsorption isotherms

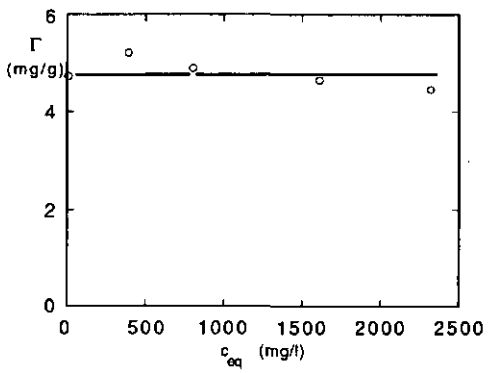

Figure 1. Adsorption isotherm of cationic amylopectin from waxy maize, DS=0.035, on microcrystalline cellulose, 0.01 M NaCl, pH=5.8, 40 g/l cellulose. Exact data are given in appendix A.1.

In figure 1 a typical adsorption isotherm for cationic amylopectin is shown, with high affinity for the surface and a clear plateau value, as is expected for polyelectrolyte adsorption [28, 29]. Since we are dealing with high affinity isotherms, a change in affinity (the initial slope of an adsorption isotherm) is very difficult to measure. The quantity that changes is the plateau value and this can be determined very well. In the following, therefore, we only show how the plateau value changes under different conditions.

4.3.2 Effect of simple electrolyte on the plateau value

The plateau value of the adsorption of cationic amylopectin as a function of the NaCl concentration shows a maximum (figure 2). This is remarkable, since the adsorption of polyelectrolytes on oppositely charged surfaces is usually found to increase [28, 29] and decreases only

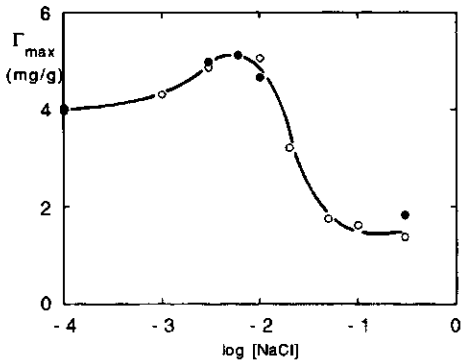

Figure 2. The effect of NaCl concentration on the plateau value of adsorption of cationic amylopectin (waxy maize, DS=0.035) on microcrystalline cellulose. pH was not set (surface charge is constant), equilibrium pH varied from 6.5 (10^{-4} M NaCl) to 5.2 (0.3 M NaCl). The open and the closed circles are from two different experiments. Values are given in appendix A.1.

occasionally [30-34]. However, Bates [23], Bonekamp [29, 35], Tanaka et al. [11] and Lindström and Wågberg [36] also found such a maximum, i.e. for polyamide-epichlorohydrin on cellulose fibers, polylysine on silica, adsorption of polyDMDAAC (poly-DiMethylDiAllylAmmonium Chloride) on cellulose fibers and for cationic polyacrylamide (c-PAM) on cellulose fibers.

Lindström and Wågberg [36] suggest that, for c-PAM on cellulose fibers, at first the adsorption increases with increasing salt concentration due to shrinking of the polyelectrolyte (screening of repulsion between the segments), so that more molecules can adsorb, and decreases with further increasing salt concentration because the electrostatic attraction between polyelectrolyte and surface is screened.

The initial increase in adsorption with increasing salt concentration could also be explained by an increase in available surface area due to the presence of pores in cellulosic material. The average pore diameter in swollen cellulose fibers is of the order of 50 Å [37, 38], which means that uncharged molecules (for instance dextranes) with $M_w > 1.1 \cdot 10^4$ are excluded. Polyelectrolytes might be able to enter these pores if they shrink enough with increasing salt concentration and, therefore, increase the adsorbed amount. Of course this effect depends on the molecular weight and structure of the polyelectrolytes.

Whether or not the latter explanation was applicable to our system, was investigated with the following experiment. Solutions of cationic amylopectin were centrifuged (4 hours, 48,400*g*) so that molecules with

sedimentation coefficients equal to or larger than 200 S[4)], which corresponds [39] to molecular weights larger than 10^7, were on the bottom of the centrifuge tubes. About 20% of the total amount of amylopectin molecules remained in the supernatant and therefore had a smaller molecular weight. With the largest amylopectin molecules the plateau adsorption as a function of the NaCl concentration was determined and again a maximum was found to appear at 0.01 M NaCl. Hence, the increase in adsorbed amount when increasing the NaCl concentration from 10^{-4} M to 10^{-2} M for the very large amylopectin molecules (hydrodynamic radius of about 100 nm, see section 3.2.7) is not caused by an increase in available surface area. From the marked decrease in viscosity of cationic amylopectin solutions with increasing salt concentration and from the decrease in hydrodynamic radius with increasing salt concentration (see section 3.2.7), as measured by dynamic light scattering, it is clear that the molecules possess enough flexibility to shrink. Therefore the initial increase in adsorption of cationic amylopectin with increasing salt concentration is due to shrinking only, and not to a change in the accessible surface area.

Even at the highest NaCl concentration, some cationic amylopectin stays adsorbed on the cellulose, which is an indication that nonelectrostatic interactions also play a role in the adsorption. Pelton [31] studied the displacement of c-PAM from cellulose fibers with La^{3+}, Ca^{2+} and Na^{+}, and found that none of them could displace the polyelectrolyte completely, and that cations with the highest valency were most effective. Lindström and Wågberg and Tanaka et al., also found that a small amount of c-PAM and polyDMDAAC, respectively, stayed adsorbed on the cellulose fibers at salt concentrations of about 1 M. The reason is probably that salt cations can not displace the adsorbed uncharged parts of the polyelectrolyte (only 3.5 monomers out of 100 bear a charged group), because the nature of the interaction between these parts and the cellulose surface is not electrostatic, and/or the specific interaction between polyelectrolyte and surface is stronger than that between salt cations and surface.

4.3.3 Effect of type of electrolyte

After the maximum, the decrease in the adsorbed amount with increasing electrolyte concentration, as shown in figure 2, is caused by two effects. The first is the screening of the electrostatic attraction between polyelectrolyte and surface. There is also a second effect, related to the finite volume of the ions and a possible nonelectrostatic interaction

[4)]S: the Svedberg unit equals 10^{-13} s.

Table 1. Effect of type of monovalent salt cation on the plateau values Γ_{max} of the adsorption of cationic amylopectin on microcrystalline cellulose.

salt cation	salt anion	Γ_{max} in 0.01 M (mg/g)	Γ_{max} in 0.02 M (mg/g)
Li^+	Cl^-	5.8 ±0.3	4.3±0.1
Na^+	Cl^-	4.9 ± 0.1	3.9 ± 0.1
K^+	Cl^-	5.2 ± 0.1	4.0 ± 0.1
Cs^+	Cl^-	4.8 ± 0.1	3.5 ± 0.1

between the ions and the surface. Salt ions not only screen charges, but the salt cations are also able to *displace* the charged polyelectrolyte segments. At high salt concentration the small ions are more effective in compensating the surface charge than the macro-ions. To check whether the salt influence on the adsorption originated from the cations indeed, we investigated the effect of replacing both the salt anion, NO_3^- for Cl^-, and the cation, Na^+ for K^+ or Cs^+. We found no effect when changing the salt anion, but changing the cation had a definite effect. In table 1, we compare the adsorbed amount of cationic amylopectin in the presence of two different salt concentrations, for Li^+, Na^+, K^+ and Cs^+.

At low salt concentration (0.001 M, not shown) the type of cation hardly affected the adsorbed amount, since screening is negligible and the small amount of cations is unable to compete with the polyelectrolytes for the charged sites on the surface. However, there is a pronounced effect for the adsorbed amounts at higher salt concentrations (0.01 M and 0.02 M). These concentrations were chosen because in this region the adsorption decreases most. The Cs^+-ions, the cations with the smallest hydrated radius, suppress the adsorption best, Li^+-ions, with the largest hydrated radius, suppress it least. In other words, the specific adsorption of Cs^+ is the highest, caused by its relatively easy loss of hydration water [40], while that of Li^+ is the lowest. Similar lyotropic series ($Cs^+ > K^+ > Na^+ > Li^+$) have been found for other systems: for oxidized cotton linters [41], for ion exchangers with carboxylate groups [42] and for charge reversal of some colloids with carboxylate groups by salt ions [43], but also for specific adsorption of these ions on a negative AgI-surface [44, 45].

4.3.4 *Effect of pH and electrolyte concentration on the plateau value*

The adsorbed amount increases with increasing pH (figure 3), which was also found for cationic starch [9, 13, 15] and for several synthetic cationic polyelectrolytes [36, 46-54]. This is expected since the surface

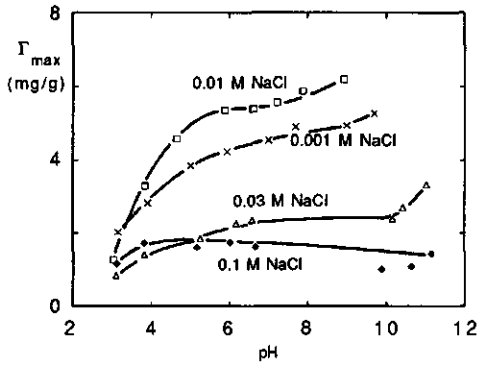

Figure 3. The influence of (equilibrium)pH on the plateau value of the adsorption of cationic amylopectin (waxy maize, DS=0.035) on microcrystalline cellulose, at different NaCl concentrations.

charge of cellulose, due to dissociation of carboxylate groups, also increases with pH (see section 3.1.6). Introduction of extra carboxylate groups on cellulose was also found to result in higher adsorption for cationic starch [8] and for several synthetic cationic polyelectrolytes [55-58]. The effect of the salt concentration on the adsorption of cationic amylopectin is the same as in figure 2 and is largest at 0.01 M. Only at the highest salt concentration, does the increase of pH have no effect, indicating that the adsorption under these conditions is not caused by electrostatic interaction. Even at pH=3, where the charge of the bare cellulose surface is almost zero, some cationic amylopectin adsorbs irrespective of the salt concentration. This may also be an indication that nonelectrostatic interactions play a role in the adsorption. Another possibility, suggested by Wågberg et al. [54], is that charge interactions are still important at low pH, because the presence of a large cationic polymer, like cationic starch, near the surface facilitates the dissociation of the COOH groups at low pH ($pH<pK_a$). The adsorbed amount of cationic amylopectin at pH=3, ±1.5 mg/g, is of the same order of magnitude as found for the adsorption on cotton linters of cassava (0.8 mg/g) and wheat amylopectin (2.4 mg/g) [26], but lower than for the adsorption of corn amylopectin on cotton linters (6 mg/g) measured by Pearl [25].

At 0.01 M NaCl, the adsorbed amount of cationic amylopectin is about 20% of the surface charge (the *bare* surface, as determined from potentiometric titrations, see section 3.1.6) at pH=5 and about 12% at pH=7. For the other salt concentrations this part is lower. Since the charge of the bare surface may differ from that in the presence of a large

polyelectrolyte (see above), the compensation of a larger part of the surface charge at pH=5 than at pH=7 is probably only apparent. The adsorbed amount of the highly charged polyDMDAAC ($M_w \approx 3.8 \cdot 10^5$) on carboxymethylated cellulose in 0.01 M NaCl was also found to compensate a larger part of the charge determined by conductometric titrations at pH=5 (25%) than at pH=7 (18%) [54]. We therefore assume that cationic amylopectin compensates about 12% of the total surface charge whereas polyDMDAAC compensates 18% of this charge. Marton and Marton [8] made a similar observation. They estimated that only about 10% of the COOH groups which were available to a low molecular weight surfactant participated to bind the quaternary ammonium groups of cationic starch (no salt added, pH=5). Both Marton and Marton, and Wågberg et al. related this limited charge compensation to the porous nature of cellulose fibers, which is why only part of the titratable charge is accessible for large molecules. The adsorption of two polyDMDAAC's, differing in molecular weight (respecively $3 \cdot 10^4$ and $1.1 \cdot 10^6$), on microcrystalline cellulose at pH=7, revealed that for neither the surface charge, as measured by potentiometric titrations, was completely accessible. The largest polyDMDAAC "saw" only one third of the charge "seen" by the smallest polyDMDAAC (see section 3.1.7), which means that at this pH about 10% of the titratable charge is available for the largest polyelectrolyte and probably also for cationic amylopectin.

4.3.5 Comparison with model calculations

Model calculations on polyelectrolyte adsorption can be very useful for the interpretation of our experimental results. We used the recent model for polyelectrolyte adsorption by Böhmer et al. [27], based on the model of Scheutjens and Fleer for polymer adsorption [59, 60]. As described in chapter 2, two regimes can be distinguished in polyelectrolyte adsorption, the *screening-enhanced adsorption* and the *screening-reduced adsorption* regime. In the former, the adsorption increases with increasing salt concentration due to screening of the repulsion between the polyelectrolyte segments, provided the short-range, nonelectrostatic interaction between polymer and surface is strong enough. In the latter regime the adsorption decreases with increasing salt concentration due to screening of the electrostatic attraction between polyelectrolyte and surface. A maximum in the adsorbed amount as a function of the salt concentration was found for the *screening-enhanced adsorption* regime, in combination with specifically adsorbing counterions. This means that in the Böhmer-model, shrinking of the polyelectrolyte due to increasing salt

concentration only, in combination with screening of the attraction to the surface, can not explain the maximum.

We tried to fit our experimental results with the Böhmer-model and a possible fit is given in figure 4a. The values of parameters chosen for this fit and the motivation for these values, are the following. The surface charge density was chosen as -0.01 C/m^2, since if all carboxylate groups are dissociated (which is the case in the experiment), the charge on microcrystalline cellulose is about -1 C/g, and the specific surface area is estimated to be 50-100 m^2/g (see section 3.1.7). In the model, a lattice site either contains a polymer segment, supposed to be a monomer, an ion or a cluster of solvent molecules. The lattice spacing determines the volume of a lattice site and we have chosen this as 0.6 nm, which is a value between the diameter of an ion (≈0.3 nm) and a glucose unit (≈1 nm). The solvent was modelled as a θ-solvent (Flory-Huggins interaction parameter χ=0.5), since water is a rather poor solvent for native starch. The strength of the nonelectrostatic, short-range interaction with the surface is represented by a χ_s-parameter, defined by Silberberg [61]. We have two of these, one for the segments (χ_{sP}) and one for the cation (χ_{sC}). The segment charge and the interaction parameters χ_{sP} and χ_{sC} were varied to obtain the best fit to the experimental results, with the restriction that neither of them should be too large. In the

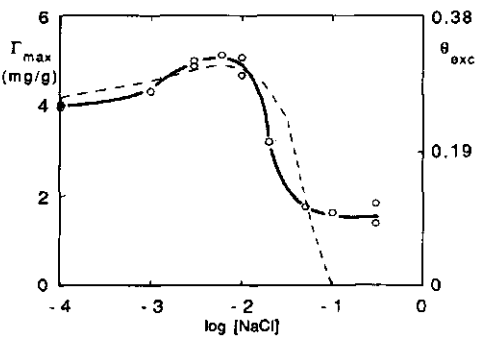

Figure 4a. Comparison of experimental results from figure 2 (open circles) with calculations (Böhmer-model, dotted line). Chain length=500, segment charge=0.1, surface charge density=-0.01 C/m^2, χ_{sP}=0.6, χ_{sC}=4. Other parameters see text. The excess adsorbed amount θ_{exc} is given in equivalent monolayers.

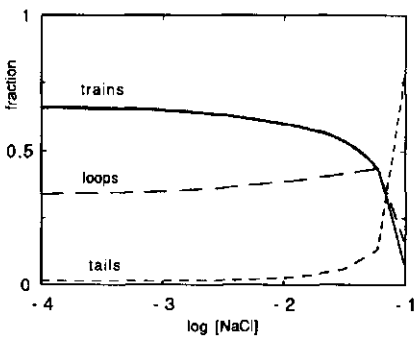

Figure 4b. Structure of the adsorbed layer, from the model calculations (figure 4a), as a function of salt concentration. The amounts of trains, loops and tails are given as fractions of the adsorbed amount.

experimental system the charge per segment is 0.035 and $\chi_{sP}>0$, as discussed before. We obtained the best fit with 0.1 charge/segment, $\chi_{sP}=0.6$ and $\chi_{sC}=4$. Due to exceedingly long computation times for longer chains, the chain length in the model calculations was chosen to be 500 segments, but the trends are the same for longer chains.

The trends of the experimental results are quite well reproduced by the model calculations (figure 4a). Initially the (calculated) adsorption increases with increasing salt concentration, like in the experiment, and then it steeply decreases to zero. The latter is not the case in the experiment. The height of the maximum is slightly smaller than in the experiment. The model calculations also give information on the conformation changes of the polyelectrolyte as a function of the salt concentration (figure 4b). As long as the salt concentration is not too high, the polyelectrolyte is attached to the surface with a large amount of trains, and about an equal amount of loops. The fraction of tails dramatically increases at high salt concentration, so with increasing salt concentration the trains and loops become smaller and smaller, until only tails are left. Van der Beek [62] has been able to experimentally detect the gradual decrease in relative train density during displacement of polymers. At the salt concentration of the maximum, the fraction of trains has somewhat decreased compared to that at lower salt concentration, and the fraction of loops has increased, so the polyelectrolyte has indeed shrunk and adopts a more extended conformation.

The Böhmer-model deals with flexible, homodisperse, linear polyelectrolytes, whereas cationic amylopectin is branched, heterodisperse and has a very large molecular weight. However, Scheutjens [63] has shown that the adsorption behaviour of star-like branched polymers hardly differs from that of linear polymers. There is a slight tendency for branched polymers to adsorb better than linear polymers, since they loose less conformational entropy. The flexibility of cationic amylopectin might be overestimated in the model, but the molecule possesses enough flexibility to shrink with increasing salt concentration, so the trends in the calculations will be correct. The polydispersity of amylopectin probably only leads to selective adsorption of the largest molecules with increasing equilibrium time [64]. Hence, the trends of the adsorption behaviour of cationic amylopectin will probably be the same as for the polyelectrolyte in the model. The surface of microcrystalline cellulose is, of course, not a smooth model surface either, but it is heterogeneous, rough and probably also porous, which means that for small ions the accessible surface area and accessible surface charge are larger than for cationic amylopectin. Moreover, the

charge of the model surface is not localised, but smeared out because of the mean field approximation. These idealisations of the model, as far as the surface is concerned, can be partly accounted for by using effective values of the interaction parameters of polymer and ions with the surface, as we will discuss below.

The necessity of a specific interaction between counterions and surface to obtain a maximum in the adsorbed amount as function of the salt concentration in the model calculations, is supported experimentally by the effect of the different types of monovalent counterions. The value of 4 for χ_{sC} necessary to fit the experimental results, is of the same order of magnitude as the adsorption energy for Li^+ and Rb^+ on a negatively charged AgI surface, found by Lyklema [44] to be 2 and 3 kT, respectively. This value might also be related to the difference in available surface charge for cationic amylopectin and the salt cations. If we assume that cationic amylopectin "feels" the charge of carboxylate groups on the cellulose in pores which it can not reach, and the salt cations can approach these charges more closely, part of the surface charge is effectively screened by the salt ions. This is reflected in the model as a loss in specific affinity of the polyelectrolyte for the surface, or an increase in the specific interaction between salt cation and the surface. So χ_{sC} probably not only represents "chemical" affinity, but also a physical "affinity" due to an advantageous difference in size.

The fit differs from the experimental results in two respects. The first is the height of the maximum, the second is the complete displacement of the polyelectrolyte by salt in the model. These two features are correlated, because it was not possible to obtain for one value of χ_{sP} simultaneuously 1) a large maximum, 2) a steep decrease in adsorption between 0.01 M and 0.1 M "NaCl", and 3) some adsorption left at the highest salt concentration. The calculations in figure 4a are such that 2) is fullfilled, so the maximum was smaller and the adsorbed amount at high salt concentration was zero. This can be understood by the following. The *height* of the maximum in the model mainly depends on the segment charge. If χ_{sP} has a certain value, the segment charge should neither be too high nor too low so as to make the adsorbed amount increase with increasing salt concentration due to screening of the repulsion between the segments. For very low or very high segment charges, the screening of the repulsion will, respectively, hardly affect the adsorbed amount, because the repulsion between the charged segments is so small that screening hardly affects the conformation, or only become visible at rather high salt concentration, because the repulsion between the segments is very large so that much salt is needed for screening this. The

increase of the adsorption with increasing salt concentration is highest for an intermediate value of the segment charge, and usually increases most between 0.01 M and 1 M salt. This means that the specific interaction of the salt cation with the surface has to be large enough to suppress this increase. The *position* of the maximum therefore depends on χ_{sC} and the segment charge. If χ_{sC} has a high value, it means that the cations are able to displace the polyelectrolyte at a low salt concentration, so the maximum occurs at low ionic strength. The segment charge should not be too low, otherwise the interaction of the polyelectrolyte with the surface is dominated by nonelectrostatic interactions, through which it is more difficult to displace the polyelectrolyte at not too high values of χ_{sC}. The partial displacement of cationic amylopectin at high NaCl concentration is not reproduced by the model, because if χ_{sC} is large enough to induce a steep decrease in the adsorption between 0.01 M and 0.1 M salt, it automatically results in a complete displacement of the polyelectrolyte by the counterions at (very) high salt concentrations.

Probably both features are related to the smearing out of the charges (mean field approximation) on the polyelectrolyte and the surface in the Böhmer-model, which in a real system only occurs at low electrolyte concentrations when the diffuse double layers are thick. Of a low charged real polyelectrolyte, a copolymer of charged and uncharged segments, some segments have a charge, whereas others have none, and at any salt concentration the uncharged part of the polyelectrolyte chain can form loops and tails more easily, giving rise to a larger maximum. In a system with localised charges, salt ions are especially able to displace charged segments and can hardly displace uncharged segments, so a part of the polyelectrolyte could stay attached to the surface. This might mean that cationic amylopectin could, even at high salt concentration, be effective if used for flocculation.

As we have already seen, the model calculations give information on the structure of the adsorbed layer. Since the polyelectrolyte in the model is linear and flexible, this is probably not fully applicable to the branched amylopectin. However, by considering the (possible) size and shape of the amylopectin molecules, as determined by Callaghan et al. [65] with NMR diffusion measurements, we have alternative possibility to visualize the adsorbed layer. Callaghan et al. obtained indications that the (effective) shape of amylopectin in aqueous solution is an oblate elipsoid or, in other words, a pancake (see also section 6.3). They estimated that the length of the short axis of this pancake is about 15 nm, and that the long axis is about 120 nm (M_w between 10^7 and 10^8). If the pancakes adsorb flat on the surface, we can estimate the fraction of the surface area covered with

cationic amylopectin. Using the length of the long axis, Γ_{max}=5 mg/g, $M_{w,ap}=5\cdot10^7$ (see section 3.2.6) and a specific surface area for microcrystalline cellulose of 6 m^2/g (see section 3.1.7), the fraction would be 50%. This means that, for pancakes, the surface is, effectively, completely covered. It should be noted that the preceding calculation can only be approximate, since the molecular weight of amylopectin (heterodispersity) and the specific surface area of microcrystalline cellulose are not exactly known. The picture of the adsorbed layer which emerges is a "mono"layer of pancakes lying on their flat side. The thickness of this layer (the "height", or the smallest diameter, of the pancake) is then about 30 nm. On the one hand this value is rather low when compared to those reported for polyelectrolytes. For instance, Wang and Audebert [34] found, for highly charged (segment charge τ=1) cationic polyacrylamide with $M_w\approx10^6$ adsorbed on silica, a hydrodynamic layer thickness of about 100 nm ($\Gamma_{max}\approx1$ mg/m^2), and for lowly charged (τ=0.01) c-PAM, with the same molecular weight, about 230 nm ($\Gamma_{max}\approx5$ mg/m^2). On the other hand we are dealing with branched polymers, which form more compact layers than linear polymers with the same molecular weight. Since the preceding is merely speculative it would be interesting for future research to investigate the thickness and structure of the adsorbed layer.

4.4 Conclusions

The adsorption of cationic amylopectin on microcrystalline cellulose as a function of [NaCl] shows a maximum. The appearance of this maximum can be explained by two opposing effects:

1. The adsorbed amount increases with increasing electrolyte concentration due to screening of the charges on the polyelectrolyte. This is only possible if the nonelectrostatic affinity of the polyelectrolyte for the surface is high enough.
2. At high electrolyte concentration the salt cation displaces the cationic groups of the polyelectrolyte from adsorption sites and therefore the adsorbed amount decreases. This displacement results from a specific (nonelectrostatic) interaction of the salt cation with cellulose.

The trends of the experimental results are reproduced quite well by model calculations based on a recent theory for polyelectrolyte adsorption. The smearing out of the charges, both on the surface and the polyelectrolyte, in the mean field approximation is probably the reason that some features of the experimental results are not reproduced completely. From the model calculations it follows that the occurrence of

a maximum in the adsorption as function of the salt concentration cannot be explained by shrinking of the polyelectrolyte with increasing salt concentration only, but both the polyelectrolyte and the counterions must have a nonelectrostatic affinity for the surface. This conclusion is further substantiated by the fact that different alkali metal ions showed different displacement strengths ($Li^+ < Na^+ \approx K^+ < Cs^+$), which is exactly what is expected for the surface affinity in this lyotropic series.

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5. ADSORPTION OF CATIONIC POTATO STARCH ON MICROCRYSTALLINE CELLULOSE

5.1 Introduction

In the previous chapter we have investigated the adsorption of cationic amylopectin from waxy maize as a first step in the fundamental understanding of the adsorption of cationic starch. However, generally starches contain two components, namely amylose and amylopectin. Cationic potato starch and cationic corn starch are mostly applied in papermaking [1], so in a study about the adsorption mechanism of cationic starch on cellulose one of those two should be used. Papermakers agree upon the superiority of (cationic) potato starch as a wet-end additive for paper [2]. Vander Burgh [3] even claims that in rosin sized[1)] cationic potato starch is twice as effective grades as cationic corn starch. The reason for this might be the combination of negatively charged phosphate groups, which are present in native potato starch but not in corn starch, and aluminium sulphate (*papermaker's alum*), which is used in rosin sized grades at a pH of about 5. At this pH, cationic aluminium hydroxide complexes are present, which might form bridges between the negatively charged phosphate groups and the negatively charged cellulose fibers, thus improving the retention of cationic potato starch. Harvey [4] showed that the retention of native potato starch in an acid furnish (pH=5) containing alum is much better than that of native corn starch indeed, but he also showed that cationic potato starch and amphoteric corn starch (cationic starch with extra phosphate groups) are equally well retained under these circumstances. For a laboratory study potato starch has two advantages compared to corn starch, namely the ease with which it can be dispersed and the lesser tendency of potato starch solutions to retrograde [5, 6]. Therefore we used cationic potato starch to study its adsorption on cellulose.

Potato starch contains about 21% amylose and 79% amylopectin [5]. Therefore, the behaviour of those components separately deserves attention. Pearl [7] has found that, at the same adsorbed amount, amylopectin improved paper strength twice as much as amylose did. This was confirmed by Isabell et al. [8] and McKenzie [9], but not by Cushing [10]. McKenzie showed that the adhesion of amylose films to cellulose fibers was poorer than the adhesion of amylopectin films, whereas the cohesion in amylose films was better than in amylopectin films, so he related the larger strength improvement by amylopectin to its better

1)rosin size: a rosin soap, which, with the added alum, gives the resulting paper a degree of water resistance.

adhesion. However, this difference was not considered commercially interesting [2].

On the other hand, any difference in adsorption behaviour between amylose and amylopectin is interesting from a fundamental point of view. It is well known to starch researchers that amylose adsorbs preferentially on cellulose [11], since they have tried to use this for fractionation purposes. However, in most studies, usually by researchers in papermaking, this difference has been neglected, except by Pearl [7]. He found that native corn amylose adsorbed much better on cotton linters than native corn amylopectin. In this study we will pay special attention to the adsorption of amylose and amylopectin from cationic potato starch separately.

It was shown in the previous chapter that charge interaction is the main driving force for adsorption of cationic amylopectin on microcrystalline cellulose. Based on the increase in adsorption by increasing the amount of carboxylate groups on the cellulose fibers, Marton and Marton [12] came to the same conclusion for cationic potato starch. These and other results about the adsorption of cationic potato starches with quaternary ammonium groups on cellulose reported in literature[2)] are summarized in table 1. To facilitate the comparison between the results obtained with cationic starch with different DS, we have calculated the adsorbed amount of charge, σ_{ads}. The plateau values of σ_{ads} measured by Marton and Marton [12], Marton [13], Harvey [4] and Krogerus [14] are about the same. The values found by Krogerus are slightly higher than those found by Marton [12, 13], which is probably due to the higher pH used by Krogerus. The effect of DS on the adsorbed amount in mg/g, reported by Krogerus, is remarkable. This can be explained by the fact that the plateau value is determined by electrostatic interactions only, as is usually the case at very low salt concentrations (see also chapter 2), since then the adsorbed amount exactly compensates the (accessible) surface charge. If the charge per segment (DS) increases, the adsorbed amount of the polyelectrolyte decreases. In an earlier study about the adsorption of cationic potato starch (DS=0.035) on microcrystalline cellulose [15], we reported a plateau value of 18 mg/g, or σ_{ads}=3.9 meq/g, in 2 mM NaCl, pH=5. This is somewhat less than reported by Marton and Krogerus, which might be due to the higher salt concentration, as we will see in section 5.3.3. The values obtained by retention measurements are all lower, since the initial concentration (1 or 2% of dry fiber weight) was probably not high enough to reach the plateau value.

[2)] a review about the adsorption of cationic starch on cellulose is given in section 4.1.

Table 1. Adsorbed amounts for cationic potato starches with quaternary ammonium groups from literature.

pH	DS	type of cellulose	Γ_{max} (mg/g)	σ_{ads}[1] (meq/g)	measured by[2]	reference
5	0.054	α-cellulose	15	5	AI	Marton & Marton [12]
5	0.054	MCC[3] ø 20 μm	8	2.7	R (2%)	Marton & Marton [12]
5	0.054	70/30 hardwood/ softwood fibers	16	5.3	AI	Marton [13]
8	0.044	furnish[4]	16	4.3	AI	Harvey [4]
7	0.023	sulphate pine fibers	9.5	1.3	R (1%)	Roberts et al. [16]
7	0.025	bleached fibers	35	5.4	AI	Krogerus [14]
7	0.05	bleached fibers	17.5	5.4	AI	Krogerus [14]

[1] σ_{ads}= adsorbed charge, calculated from: $\Gamma_{max} \cdot DS/162$, 162 is the molecular weight of a glucose unit.
[2] AI=adsorption isotherm, R=retention, (x%): amount of cationic starch added on fiber dry weight.
[3] MCC= microcrystalline cellulose.
[4] furnish: 75% hardwood/ 25% softwood; 2.4% titanium dioxide, 9.6% calciumcarbonate.

Here we will study the adsorption of cationic potato starch on microcrystalline cellulose and we will pay attention to the adsorption of amylose and amylopectin separately. We will also investigate the influence of pH, simple electrolyte concentration, cellulose concentration and degree of substitution (DS) of the starch, on the adsorption. Microcrystalline cellulose was used as a model for cellulose fibers. Some preliminary results of our study on the adsorption of cationic potato starch are already published [15].

5.2 Experimental

As described in chapter 3 of this thesis.

5.3 Results and discussion

5.3.1 Starch: a mixture of amylose and amylopectin

In order to study the adsorption of cationic amylose and cationic amylopectin separately, we fractionated cationic potato starch (DS=0.035) by ultracentrifugation, taking advantage of the large difference in molecular weight between amylose and amylopectin (for details see section 3.2.9). We obtained an amylose-rich fraction (AM) with 67.5% amylose, and an amylopectin-rich fraction (AP) with 3% amylose. The adsorption of AM and AP on untreated microcrystalline cellulose was compared with that of cationic potato starch (ST), with 21% amylose, under the same circumstances. The equilibrium concentrations were analysed on total carbohydrate content and amylose/amylopectin content (see sections 3.3 and 3.4). In figure 1 the adsorbed amounts of total carbohydrate, amylose and amylopectin from ST, are given as function of the equilibrium carbo-hydrate concentration. If amylose and amylopectin adsorb with the same affinity, we might expect that the total adsorbed amount contains 21% amylose, like in the initial ST-solution. From figure 1 and table 2, it is clear that amylose adsorbs preferentially. This makes the concentration axis very complicated, since the ratio amylose/amylopectin in the equilibrium solution is not 0.21/0.79 anymore, but differs from point to point on the adsorption isotherm. As we can see in table 2, the adsorbed amount of amylose very soon reaches a constant level of about 30% of the total and the amylose content of the

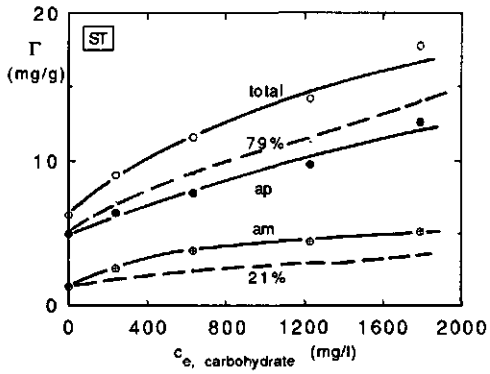

Figure 1. Adsorption of total carbohydrate (○), amylose (⊕) and amylopectin (●) from cationic potato starch (DS=0.035, denoted as ST, 21% amylose) on *untreated* microcrystalline cellulose as function of the equilibrium concentration carbohydrate, 2 mM NaCl, pH=6.5, 40 g/l cellulose. The dotted lines indicate 21% and 79% of the total adsorbed amount carbohydrate.

Table 2. Equilibrium concentrations of total carbohydrate (st), amylose (am) and amylopectin (ap) and corresponding adsorbed amounts, from cationic potato starch with 21% amylose, 2 mM NaCl, pH=6.5, DS=0.035, partly plotted in figure 1 and figures 4a,b,c.

$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	% am of $c_{e,st}$	Γ_{st} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g	% am of Γ_{st}
0	0	0	0	6.3	1.3	5.0	20.6
239	22	218	9.2	9.0	2.6	6.4	28.9
635	78	557	12.3	11.6	3.8	7.8	32.8
1231	200	1031	16.2	14.2	4.4	9.8	31.0
1790	320	1470	17.9	17.7	5.1	12.6	28.8

equilibrium solution increases from 0 to 18%. The preferential adsorption of amylose is more pronounced in all the other experiments where cleaned cellulose is used. In the these experiments (see figures 5 and 6) the adsorption of total carbohydrate at high carbohydrate equilibrium concentration is slightly lower (both plotted in figure 15 of section 3.4.1), whereas the adsorption of amylose was about the same. Therefore the share of amylose in the total adsorbed amount is larger for cleaned cellulose.

If the starch determination is sensitive to changes in the amylose/amylopectin ratio, the calibration (made with 21% amylose) is invalidated by a changing ratio of amylose/amylopectin in the equilibrium solution. A total carbohydrate determination is not susceptible to such changes, contrary to a starch determination with iodine, which is always more sensitive for amylose than for amylopectin (see section 3.3.2 for more information). Employing the latter method, the more than proportional disappearance of amylose from the initial starch solution would lead to adsorbed amounts that are too high. Therefore, adsorption measurements where starch is determined with iodine only, are questionable. However, we were aware of this problem and determined the total adsorbed amount with a carbohydrate determination. We used the sensitivity of an iodine determination for amylose in combination with the carbohydrate determination to calculate the adsorbed amount of amylose and amylopectin, as described in section 3.4.3.

What is the reason for the preferential adsorption of amylose? In general it might be related to their different molecular structures. Amylose is a flexible, essentially linear polymer, with molecular weights in the order of a few hundred thousands, and in solution it behaves as a random coil [6]. Amylopectin, on the other hand, is a branched polymer,

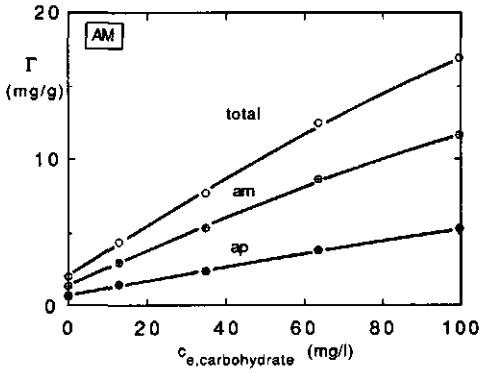

Figure 2. Adsorption of total carbohydrate (○), amylose (⊕) and amylopectin (●) from amylose-rich cationic potato starch (DS=0.035) obtained by ultracentrifugation (denoted as AM, 67.5% amylose), on *untreated* micro-crystalline cellulose as a function of the equilibrium concentration carbohydrate, 2 mM NaCl, pH=6.5, 40 g/l cellulose.

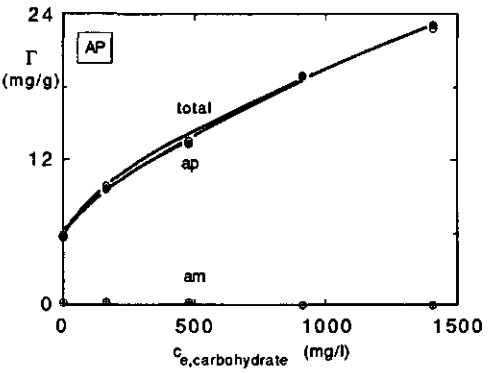

Figure 3. Adsorption of total carbohydrate (○), amylose (⊕) and amylopectin (●) from amylopectin-rich cationic potato starch (DS=0.035) obtained by ultracentrifugation (denoted as AP, 3% amylose), on *untreated* micro-crystalline cellulose as a function of the equilibrium concentration carbohydrate, 2 mM NaCl, pH=6.5, 40 g/l cellulose.

with molecular weights of a few hundreds of millions. In a good solvent it has the shape of an oblate ellipsoid [17] (like a pancake) which can shrink, giving a spheroid, if the solvent quality decreases [6]. For cationic amylopectin this means that the expanded conformation at low salt concentration is expected to be a pancake, which will shrink into a spheroid at high salt concentration.

The first more specific possibility for the preferential adsorption of amylose we consider, is different adsorption kinetics for amylose than for amylopectin, due to differences in shape and in molecular weight. From an experiment comparing the adsorption kinetics of amylose-rich and amylopectin-rich cationic potato starch, obtained by ultracentrifugation, on silica, with a reflectometric technique in stagnation point flow [18], it appeared that, per unit of concentration, the amylose-rich fraction adsorbed four times faster than the amylopectin-rich fraction. If amylose and amylopectin adsorb from a starch solution, we also have to consider their concentration in the initial solution, since the adsorption velocity, $d\Gamma/dt$, is proportional to $D^{2/3} \cdot c$ [18], where D is the diffusion coefficient and c the initial concentration. The concentration of amylopectin is four times larger than that of amylose, which in the product $D^{2/3} \cdot c$ exactly compensates its eight times larger diffusion coefficient, so in a starch solution we expect no difference in adsorption velocity between amylose

and amylopectin. Only if amylose reaches the surface faster than amylopectin and amylopectin can not displace amylose during an equilibration time of 15 hours, amylose might adsorb preferentially. Such an irreversible adsorption, however, can not be reconciled with the effect of changing the cellulose concentration, which will be discussed in section 5.3.2, since it appears that during 15 hours exchange between small and large molecules does take place. Therefore the difference in adsorption kinetics can not explain the preferential adsorption of amylose.

An unequal distribution of cationic groups over amylose and amylopectin could also be an explanation for the preferential adsorption of amylose. Recently, Salomonsson et al. [19] investigated this distribution in a cationic potato starch with DS=0.03 (quaternary ammonium groups). They found that the amylopectin fraction had a DS of 0.035, whereas the amylose fraction had a DS of 0.022. This is opposite to the results of Steeneken [20, 21] which indicate that amylose is preferentially substituted (see also section 3.2.2). Steeneken attributed this to the fact that the reagents, penetrating the granule, can reach amylose more easily than amylopectin, since the former is located in the amorphous part of the granule, whereas the latter is crystalline. Obviously new research is necessary to judge which of the two investigators is right. The best solution would be to determine the DS of amylose and amylopectin in our cationic starch, but we have not been able to do so. Fortunately, thermodynamics helps us to predict whether amylose will adsorb preferentially if it has a higher or a lower DS than amylopectin. On entropic grounds we expect that, from a mixture of differently charged but otherwise identical polymers, the polymers with the highest charge will adsorb preferentially on an oppositely charged surface, because the system looses less entropy if the surface charge is compensated with a small amount of highly charged polymers. This means that, only if amylose has a higher charge than amylopectin and there are no other differences of importance for their adsorption behaviour, an unequal distribution of cationic groups over amylose and amylopectin can explain the preferential adsorption of amylose.

The third possibility is a larger accessible surface area for amylose than for amylopectin on the probably porous (see par 3.1.7) microcrystalline cellulose. Tanaka et al. [22] found that the adsorption of lowly charged cationic polyacrylamides with molecular weights of $4 \cdot 10^5$ and $8 \cdot 10^6$, on cellulose fibers, as measured after about 30 min, increased with 50% during 17 hours equilibration time, whereas the adsorption of the same polyelectrolytes on a negatively charged latex did not change at all. This

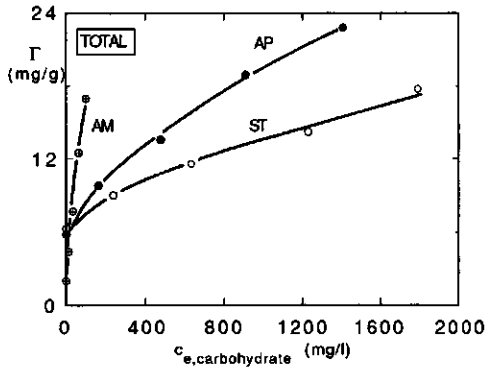

Figure 4a. Combination of the experiments in figures 1-3. Adsorption of *total carbohydrate* as a function of equilibrium concentration *total carbohydrate*, from cationic potato starch (ST, 21% amylose, o), amylose-rich cationic potato starch from ultracentrifugation (AM, 67.5% amylose, ⊕) and amylopectin-rich cationic potato starch (AP, 3% amylose, ●), 2 mM NaCl, pH=6.5, 40 g/l cellulose, DS=0.035.

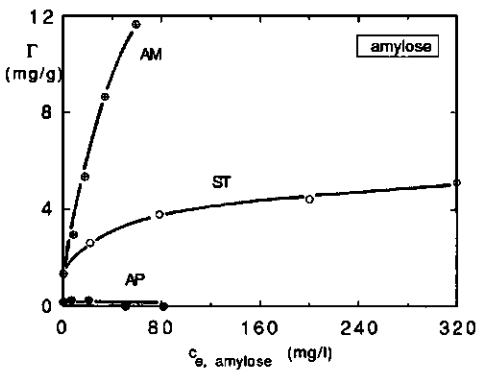

Figure 4b. Combination of the experiments in figure 1-3. Adsorption of *amylose* as a function of equilibrium concentration *amylose*, from cationic potato starch (ST, 21% amylose, o), amylose-rich cationic potato starch from ultracentrifugation (AM, 67.5% amylose, ⊕) and amylopectin-rich cationic potato starch (AP, 3% amylose, ●), 2 mM NaCl, pH=6.5, 40 g/l cellulose, DS=0.035.

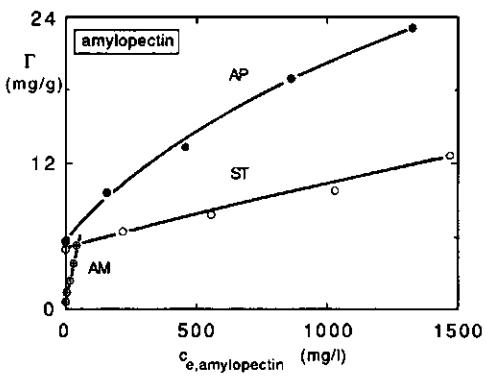

Figure 4c. Combination of the experiments in figure 1-3. Adsorption of *amylopectin* as a function of equilibrium concentration *amylopectin*, from cationic potato starch (ST, 21% amylose, o), amylose-rich cationic potato starch from ultra-centrifugation (AM, 67.5% amylose, ⊕) and amylopectin-rich cationic potato starch (AP, 3% amylose, ●), 2 mM NaCl, pH=6.5, 40 g/l cellulose, DS=0.035.

increased adsorption was attributed to slow penetration of the polymers into the pores, so it is indeed possible that the available surface area of microcrystalline cellulose is larger for the smaller and linear amylose than

for the large and branched amylopectin. The adsorption of cationic amylopectin from waxy maize on microcrystalline cellulose after 30 min was the same as after 17 hours (chapter 4), which indicates that amylopectin can not enter the pores. We may conclude that the presence of pores in microcrystalline cellulose, which can be entered by the smaller and linear amylose molecules, seems the best explanation for the preferential adsorption of amylose.

Now we will examine whether the results of the adsorption experiments with the amylose-rich cationic potato starch (AM) and amylopectin-rich cationic potato starch (AP) in figures 2 and 3, are in agreement with this hypothesis. In both cases, the adsorbed amount of amylose is proportional to the amount in the initial solution (values are given in appendix A.2). This is understandable for AP, since the amount of amylose in the initial solution is so small that it can not compete with the much larger amount of amylopectin. Moreover, such small amounts of amylose are difficult to detect, causing a large experimental error. For AM, it seems strange at first, that about 67% of the total adsorbed amount is amylose, like in the initial solution, since we expect amylose to adsorb preferentially due to its higher initial concentration. We have to realize that AM was obtained by ultracentrifugation, which means that the amylopectin in this solution will have a molecular weight comparable to that of amylose. In that case the preference of amylose for the surface has disappeared because smaller amylopectin molecules are also able to enter the pores. This could also explain that the adsorbed amount obtained with AM is almost as large as that obtained with ST. In addition, a preferential adsorption of amylose may not be visible yet in the adsorption isotherm of figure 2, because we are dealing with much smaller concentrations than in figure 1. We can conclude that the results in figures 2 and 3 are in agreement with the hypothesis that the preferential adsorption of amylose is related to a larger available surface area.

In figure 4 the adsorption data in figures 1-3 are combined in such a way that the adsorbed amount of a component is plotted against the equilibrium concentration of that component. Figure 4a shows that the adsorbed amount of carbohydrate obtained with a sample comprising mainly small starch molecules (AM) reaches about the same level as that obtained with normal cationic starch (ST), whereas a higher level is reached from a sample with an excess of large starch molecules (AP). The rise in the adsorption of the small molecules is probably steeper because this sample is more homodisperse. Hlady et al. [23] found steeper adsorption isotherms for homodisperse polymers than for heterodisperse samples. The fact that the adsorption level of small amylose and small

amylopectin molecules (AM) is about the same as that of ST may be caused by a larger available surface area for small molecules, as discussed before. It is not likely that these small molecules are able to create the same layer thickness as the larger molecules in ST, since this generally depends on molecular weight [24]. The higher adsorbed amount obtained by AP, might be caused by the much larger amylopectin molecules in this sample, which create a thicker adsorbed layer. From figure 4b and 4c, it is clear that both amylose and amylopectin adsorb better on cellulose if their share in the initial solution is larger, or in other words, if the competition from the other component is less.

5.3.2 Influence of cellulose concentration

In figure 5a the influence of the cellulose concentration on the adsorption isotherm of cationic potato starch is shown. It seems that cationic starch adsorbs better at the low cellulose concentration, but this effect is due to heterodispersity of the polymer sample, as was shown by Hlady et al. [23]. The influence of the surface to volume ratio on the adsorption isotherms can be explained as follows. From a mixture of polymers of the same kind, but of different chain length, the small polymers may adsorb first, but they are later replaced by the largest polymers. The driving force for the exchange is the gain in translation entropy when one large polymer takes the place of a few small polymers, which are released into solution. Since for each chain there is a fixed contribution to the translation entropy, the system gains entropy. If the

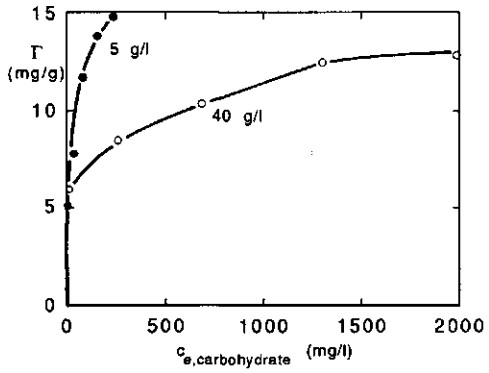

Figure 5a. Adsorption isotherms of cationic potato starch (DS=0.035) on cleaned microcrystalline cellulose, 2 mM NaCl, pH=6. o 40 g/l cellulose, ● 5 g/l cellulose.

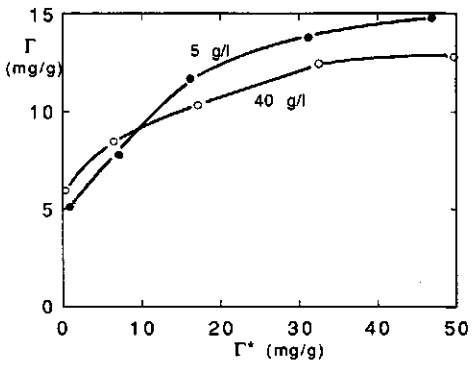

Figure 5b. The adsorbed amounts from figure 4a plotted against the nonadsorbed amount Γ* (=c_e·$c_{cellulose}$). o 40 g/l cellulose, ● 5 g/l cellulose.

solid content of the system is low, at equilibrium the available surface area will be covered by the largest polymers. Those polymers can form long loops and tails, so the adsorbed amount (in mg/g) is high, even at low polymer concentration. On the other hand, at high solid content, the surface will be covered with polymers of different chain length, since in a given volume the amount of large polymers is not large enough to replace all small polymers from the surface. If the concentration of the polymer solution is raised, more large polymers are present in the same volume and they can displace the small polymers, thereby increasing the adsorbed amount. Hence, the *amount* of large polymers in a certain volume is of importance and not the concentration. This effect on the adsorption isotherms can be eliminated if the adsorbed amount is plotted against the nonadsorbed amount Γ^* ($=c_e \cdot c_{cellulose}$), instead of the equilibrium concentration.

Since the cationic potato starch contains only 3.5 cationic groups per 100 glucose units, it will presumably, with respect to heterodispersity, in first approximation behave as an uncharged polymer. This is indeed the case, as can be seen in figure 5b where the adsorbed amount is plotted against the nonadsorbed amount. Now the two curves almost merge into one. The same can be done for the calculated adsorption isotherms of amylose and amylopectin. Plotted in the manner of figure 5b (not shown, but data are given in appendix 2), the curves for amylose and those for amylopectin also merge. This means that, since amylose nor amylopectin seems to hinder the adsorption of the other component, both the amylose and the amylopectin fraction are fairly heterodisperse.

The contribution of amylose to the total adsorbed amount was 45% in 40 g/l cellulose, and 38% in 5 g/l cellulose, so the different cellulose concentration did hardly affect the preference of amylose for the surface.

5.3.3 Influence of simple electrolyte concentration

The adsorption of cationic potato starch decreases strongly with increasing NaCl concentration (figures 6a and 7) and for [NaCl] ≥ 0.02 M (figure 7) the adsorbed amount seems to become even negative. The latter is probably due to the large experimental error in these measurements, since the initial concentration was so large (2500 mg/l, see also appendix A.2) that it was not possible to distinguish between a very small adsorbed amount (in the order of 1 mg/g) and no adsorption at all. We have called this behaviour in polyelectrolyte adsorption the *screening reduced adsorption* regime (chapter 2). The electrostatic

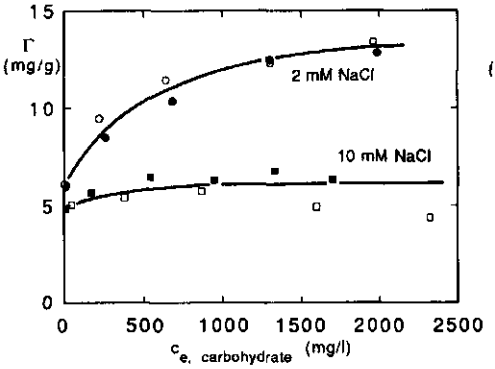

Figure 6a. Adsorption of cationic potato starch (total carbohydrate, DS=0.035) on cleaned microcrystalline cellulose as a function of the equilibrium concentration total carbohydrate, 2 mM NaCl, pH=6 and 10 mM NaCl, pH=7. The open and closed symbols denote duplicate experiments.

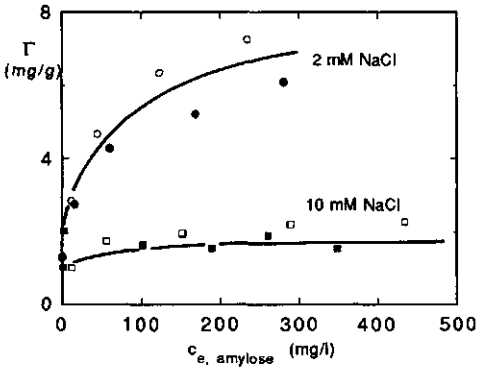

Figure 6b. Same experiment as in figure 6a, but now the adsorption of cationic amylose from cationic potato starch (DS=0.035) on microcrystalline cellulose is plotted as a function of the equilibrium concentration amylose.

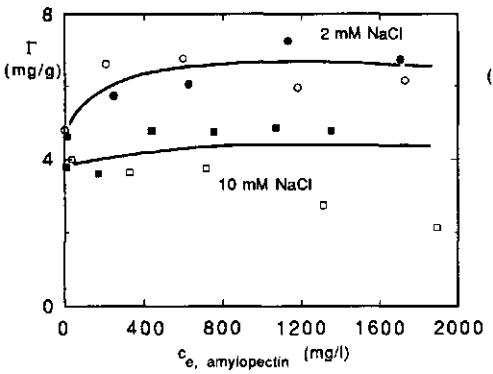

Figure 6c. Same experiment as in figure 6a, but now the adsorption of cationic amylopectin from cationic potato starch (DS=0.035) on microcrystalline cellulose is plotted as a function of the equilibrium concentration amylopectin.

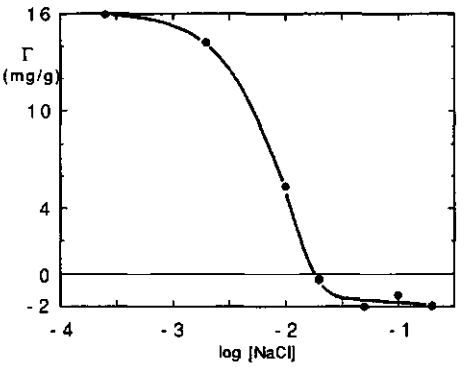

Figure 7. Plateau value of the adsorption of cationic potato starch (total carbohydrate, DS=0.035) on cleaned microcrystalline cellulose, pH was not set and varied from 7.6 for the lowest [NaCl] to 5.7 for the highest.

attraction between negatively charged cellulose and cationic starch is screened by the increasing salt concentration, and decreasing adsorption of the polyelectrolyte indicates that this interaction is the main driving force for adsorption. The same applies to the starch components (figure 6b and c). The decreasing adsorption of amylose and amylopectin in the

experiment of figure 7 is not shown, but the trend is the same (corresponding values are given in appendix 2). In section 6.3 we will compare the adsorption behaviour of cationic potato starch and its components with that of cationic amylopectin from waxy maize. The preference of amylose is less in 10 mM NaCl than in 2 mM, respectively 36% and 51% of the total adsorbed amount. It might be less favorable for cationic amylose to enter the pores, because better screening of the charges at 10 mM NaCl has two effects. Firstly cationic amylose is less attracted by the charges in the pores and secondly the conformation of cationic amylose becomes more like a random coil hindering the penetration into the small pores.

5.3.4 Influence of type of electrolyte

5.3.4.1 Monovalent cations

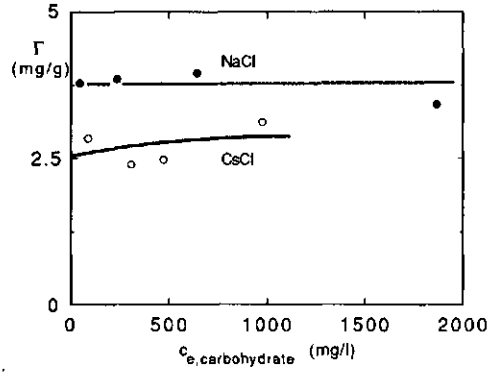

Figure 8. The adsorption of cationic potato starch (DS=0.035, total carbohydrate) on cleaned microcrystalline cellulose as a function of the equilibrium concentration carbohydrate, in 0.01 M NaCl (●) and 0.01 M CsCl (o), pH=5, 40 g/l cellulose.

From figure 8 it seems that the decreased adsorption of cationic potato starch with increasing electrolyte concentration is not only caused by

Table 3. The plateau values (total carbohydrate) of cationic potato starch (DS=0.035) adsorbing on cleaned microcrystalline cellulose, pH=5, 40 g/l cellulose.

salt cation	salt anion	Γ_{max} in 0.01 M (mg/g)
Na^+	Cl^-	3.3 ± 0.1
K^+	Cl^-	3.4 ±0.2
Cs^+	Cl^-	3.2 ± 0.2

screening, but also by specific interactions of salt cations with the cellulose surface. In the presence of Cs^+-ions, the ions with the smallest hydrated radii, less cationic starch is adsorbed than in the presence of the same concentration Na^+-ions. This indicates that the former ions have a stronger specific interaction with the negatively charged carboxyl groups caused by their relatively easy loss of hydration water [25]. However, in another experiment (table 3) it appeared that the effect of Na^+, K^+ or Cs^+ on the adsorption is practically the same. The ambiguity of the experimental results, therefore, does not allow us to draw a conclusion about specific effects of monovalent cations, but, based on the facts that K^+ adsorbs better on oxidized cotton linters than Na^+, while Na^+ adsorbs better than Li^+ [26], and that the type of cation affected the adsorption of cationic waxy maize (section 4.3.3), we would also expect these effects for the adsorption of cationic potato starch. The preferential adsorption of amylose was not affected by the type of salt cation, in all cases amylose contributed about 33% to the total adsorbed amount.

5.3.4.2 Divalent cations

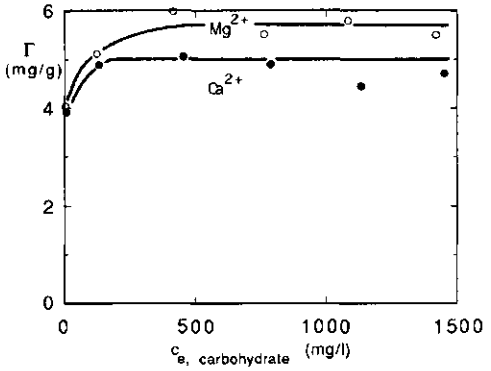

Figure 9. The adsorption of cationic potato starch (DS=0.035, total carbohydrate) on cleaned microcrystalline cellulose as a function of the equilibrium concentration carbohydrate, in 1 mM $CaCl_2$ (●) and 1 mM $MgCl_2$ (○), pH=5, 40 g/l cellulose.

If we compare the effect of 2 mM and 10 mM NaCl in figure 6a, with the effect of 1 mM $CaCl_2$ or $MgCl_2$, it is clear that at a concentration of 1 mM the divalent cations have about the same effect as 10 mM NaCl, so they are ten times as effective in decreasing the interaction between cationic starch and cellulose. The presence of 1 mM of calcium salts in process water of papermachines is not unlikely, since calcium carbonate is often used as filler, so apart from aluminium sulphate and anionic wood polymers [27], calcium ions can also be a cause for the poor retention of

starch observed in recent years. Usually, calcium ions are not included in the socalled "detrimental substances", or even "anionic trash" [32, 33].

With the Debije-length κ^{-1}, calculated from [34]

$$\kappa^2 = 5.411 \sum_j c_j z_j^2 \qquad (1)$$

where κ is in nm^{-1} and c_j is the concentration of salt ion j in moles/l, and z_j is the valency of ion j, we can determine whether or not this is simply caused by more effective screening by divalent ions. For 10 mM NaCl, κ^{-1} equals 3.04 nm, whereas it is 5.55 nm for 1 mM $CaCl_2$ or $MgCl_2$. This means that the larger effect of the divalent cations is not only caused by more effective screening, but also by some specific interaction between Ca^{2+} or Mg^{2+} and carboxylate groups. Lindström and Wågberg [35] also found for cationic polyacrylamide adsorbing on cellulose fibers such a larger influence of $CaCl_2$ on the adsorbed amount.

The adsorbed amount is a little higher in the presence of Mg^{2+}-ions than in that of Ca^{2+}-ions, indicating a somewhat stronger specific adsorption of the latter. This is consistent with the fact that Ca^{2+}-ions are slightly lesser hydrated than Mg^{2+}-ions and can therefore loose their hydration water more easily. However, this effect is smaller than the specific interactions of the monovalent cations with the carboxylate groups. Ca^{2+}-ions may also have a strong specific interaction with the phosphate groups of cationic potato starch (see also section 3.2.4), because the solubility of calciumphosphate is much smaller than that of magnesiumphosphate [36]. This is apparently no the case, since the influence of Ca^{2+}-ions on the adsorption is only slightly larger than that of Mg^{2+}-ions. Hence these phosphate groups probably do not play an important role in the adsorption of cationic potato starch.

The percentage amylose of the total adsorbed amount was about 37%, so it is comparable to the preference of amylose in 10 mM NaCl.

5.3.5 Influence of pH

The adsorbed amount increases considerably if the pH is increased (figure 10). The surface charge of microcrystalline cellulose also increases with increasing pH, being largest between pH 4 and 6 (section 3.1.6), so this is again a good indication that charge interactions play an important role. Also notice the large effect of 0.01 M HCl compared to 0.01 M NaCl. Obviously, the interaction of H^+-ions with the carboxylate groups (pK≈4) is much stronger than that of the cationic groups from the starch. The fact that the adsorbed amount at pH=2, where the surface charge is zero, is

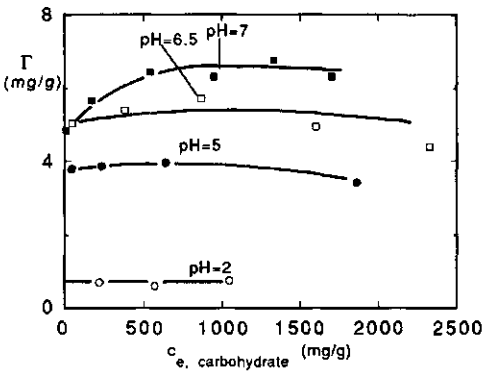

Figure 10. The adsorption of cationic potato starch (DS=0.035, total carbohydrate) on cleaned microcrystalline cellulose as a function of the equilibrium concentration carbohydrate, at pH=2 (0.01 M HCl) and in 0.01 M NaCl at pH=5, 6.5 and 7, 40 g/l cellulose.

larger than zero might indicate that some short-range, nonelectrostatic interaction is present between starch and cellulose. This is also evident from adsorbed amounts reported for uncharged (native) starch, for instance the 1.2-5 mg/g reported by Cushing and Schuman [37] for native corn starch. In our experiment the adsorbed amount at pH=2 is lower, only 1 mg/g. The reason is that a polyelectrolyte adsorbing on an uncharged surface charges the surface, so that the electrostatic repulsion prevents a further increase in adsorbed amount. The adsorption of an uncharged polymer on an uncharged surface will therefore in most cases be higher than the adsorption of a polyelectrolyte on such a surface. At a lower salt concentration, we expect that the increase in adsorption with increasing pH will be even larger, since at a salt concentration of about 0.01 M the charge interaction is more screened than in 2 mM. It is also possible that charge interactions still play a role at low pH, as suggested by Wågberg et al. [38], because the presence of a large cationic polymer, like cationic starch, near the surface facilitates the dissociation of the COOH groups at low pH ($pH<pK_a$).

Increasing adsorption with increasing pH for cationic starch was also found by [4, 16, 39], and for several other polyelectrolytes adsorbing on cellulose [35, 38, 40-47]. A comparable effect is found by increasing the carboxyl content of the cellulose fibers. Marton and Marton [12] found that this resulted in increasing adsorption of cationic starch and it was also found for several synthetic cationic polyelectrolytes [48-51].

The percentage of amylose in the total adsorbed amount, was about 34% for all pH's, so in 0.01 M NaCl the preference of amylose for the surface is not affected by pH. This is to be expected if it is less favorable

for amylose to enter the pores at 0.01 M NaCl, as we suggested in the previous section.

At pH=5 the adsorbed amount of cationic starch is about 13% of the surface charge (the *bare* surface, as determined from potentiometric titrations, see section 3.1.6) and about 12% at pH=7. The adsorbed amount of the highly charged polyDMDAAC ($M_w \approx 3.8 \cdot 10^5$) on carboxymethylated cellulose in 0.01 M NaCl was also found to compensate 25% of the bare surface charge at pH=5 and 18% at pH=7 [38]. Marton and Marton [12] estimated that only about 10% of the COOH groups which were available to a low molecular weight surfactant participated to bind the quaternary ammonium groups of cationic starch (no salt added, pH=5). Both Marton and Marton, and Wågberg et al. related this limited charge compensation to the porous nature of cellulose fibers, which is why only part of the titratable charge is accessible for large molecules. The adsorption of two polyDMDAAC's, differing in molecular weight (respecively $3 \cdot 10^4$ and $1.1 \cdot 10^6$), on microcrystalline cellulose at pH=7, revealed that for neither the surface charge, as measured by potentiometric titrations, was completely accessible. The largest polyDMDAAC "saw" only one third of the charge "seen" by the smallest polyDMDAAC (see section 3.1.7), which means that at this pH about 10% of the titratable charge is available for the largest polyelectrolyte and probably also for cationic potato starch.

5.3.6 Influence of degree of substitution

The influence of the degree of substitution (DS) of starch was investigated at 2 mM and 10 mM NaCl. The resulting adsorption isotherms are given in figures 11 and 12. In 2 mM NaCl (figure 11), the adsorbed amount of cationic starch with DS=0.017 is only 25% higher than that of starch with DS=0.047, in contrast to the factor two found by Krogerus [14] for cationic starch with DS=0.025 and 0.05. If the NaCl concentration is higher (figure 12), there is almost no difference between the adsorption of cationic starch with DS=0.017, 0.035 and 0.047 respectively, although the starches with the higher DS seem to adsorb a little better than starch with DS=0.017.

With help of model calculations on polyelectrolyte adsorption (see chapter 2), these, at first sight puzzling, results become understandable. In figure 13 the influence of 1:1 electrolyte concentration ("NaCl") on the adsorbed amount (plateau values), for a polyelectrolyte adsorbing on an oppositely charged surface is shown. The largest effect of DS occurs at the lowest salt concentration, and the adsorbed amount is inversibly proportional to the DS, since the polyelectrolyte adsorbs until the surface

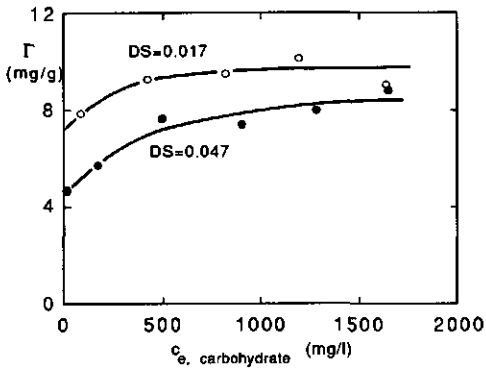

Figure 11. The adsorption of cationic potato starch (total carbohydrate) on cleaned microcrystalline cellulose as a function of the equilibrium concentration carbohydrate, for DS=0.017 (o) and DS=0.047 (●) in 2 mM NaCl, pH=5, 40 g/l cellulose.

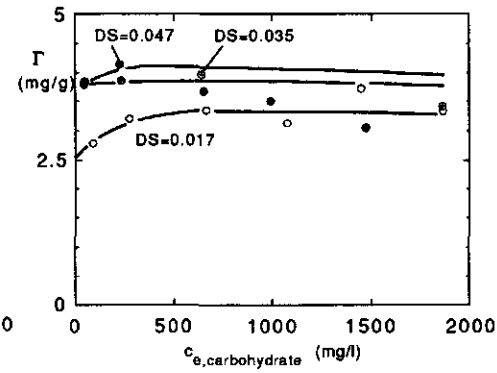

Figure 12. The adsorption of cationic potato starch (total carbohydrate) on cleaned microcrystalline cellulose as a function of the equilibrium concentration carbohydrate, for DS=0.017 (o), DS=0.035 (⊕) and DS=0.047 (●) in 0.01 M NaCl, pH=5, 40 g/l cellulose.

charge is compensated. This explains the difference between our experiments at 2 mM NaCl and those of Krogerus, since the latter did not add salt to his system. So if we would have carried our experiments at a lower salt concentration, the difference between high and low DS would have been even larger. At higher salt concentrations, the electrostatic attraction between polymer and surface is screened, and the adsorbed amount decreases. The adsorption of the polymer with the lowest charge (τ=0.015) decreases very rapidly with increasing salt concentration, because the electrostatic interaction with the surface is relatively (compared to a polymer with a higher segment charge) weak and therefore easily screened. The polymer with the highest charge (τ=0.05) has the relatively strongest electrostatic interaction with the surface, so the salt concentration must be higher for complete screening of this interaction. Between 10^{-3} and 10^{-2} M NaCl, the curves of τ=0.035 and 0.05 cross each other, so at these salt concentrations no difference between the two segment charges is found. Something of asimilar nature probably occurs in our experimental system at 10 mM NaCl.

In 2 mM NaCl, amylose constitutes 35% of the total adsorbed amount for DS=0.017 and about 37% for DS=0.047, which is remarkably lower than the 51% found for amylose with DS=0.035. This might be caused by the difference in pH between the experiments in figure 11 (pH=5) and figure 6 (pH=7). In the previous section we have seen that increasing the

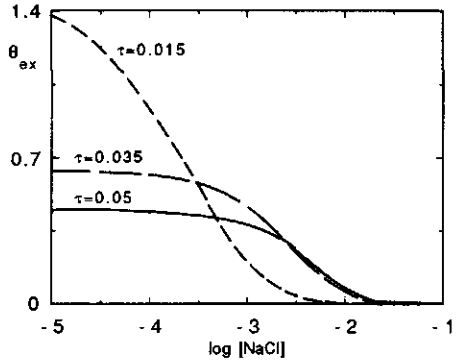

Figure 13. The influence of 1:1 electrolyte (for convenience denoted as "NaCl") on the excess adsorbed amount θ_{ex} (in equivalent monolayers) of a polyelectrolyte with 100 segments and variable relative segment charge τ, on a surface with σ_0=-0.01 C/m^2, only electrostatic interactions (χ_s=0), θ-solvent (χ=0.5) polymer volume fraction $\phi=10^{-3}$. Dielectric constants of solvent and salt ions: 80, dielectric constant of polyelectrolyte: 20, hexagonal lattice, lattice spacing 0.6 nm. More information on model calculations in chapters 2 and 4.

pH from 5 to 7, in 0.01M NaCl, leads to a considerable increase in the adsorption, due to an increasing accessible surface charge. The fraction of amylose in the total adsorbed amount was hardly affected, probably because it is less favourable for cationic amylose to enter pores at a higher salt concentration. The adsorbed amount in 2 mM NaCl is much higher than in 0.01 M NaCl, partly due to the ability of cationic amylose to enter the pores. Therefore we expect that increasing the pH from 5 to 7 in 2 mM NaCl will also increase the adsorption of amylose in the pores, which leads to a larger fraction of amylose in the total adsorbed amount.

5.4 Conclusions

From solutions of cationic potato starch (21% amylose) cationic amylose adsorbs preferentially on microcrystalline cellulose. The percentage of amylose in the total adsorbed amount is not affected by pH or type of salt cation. This can be explained by the assumption that the preferential adsorption of amylose is caused by a larger accessible surface area for amylose than for amylopectin, due to the ability of the former to enter pores in 15 hours of equilibration time. Due to this preferential adsorption of amylose, previously reported adsorption measurements where the equilibrium concentration was determined with iodine only, become questionable.

From the pronounced effect of the cellulose concentration on the adsorption isotherm, we can conclude that both amylose and amylopectin are fairly heterodisperse.

Charge interactions are important driving forces for adsorption, since adsorption decreases substantially with increasing salt concentration and increasing the pH leads to increased adsorption. Since cationic potato starch is able to overcompensate the accessible surface charge, there is also a nonelectrostatic interaction with the surface.

Divalent cations are ten times more effective in decreasing the adsorption of cationic starch than monovalent cations, due to a combination of their higher charge and some specific interaction with the surface. Therefore, calcium ions can be important detrimental substances in papermaking. The small difference between the effect of Ca^{2+} and Mg^{2+} indicates that phosphate groups are not important for the adsorption of cationic potato starch, since a stronger interaction of Ca^{2+} than of Mg^{2+} with phosphate groups is expected. The influence of DS on the adsorption of cationic starch is such, that at low salt concentration the lowest DS adsorbs best, whereas at moderate salt concentration the starch with the highest DS adsorbs somewhat better, although the differences between DS's are small. This can be explained with model calculations, which also clearly indicate that the effect of DS will be larger at smaller (<2 mM) and at higher (>0.01 M) salt concentrations than we used.

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6 CONCLUSIONS

6.1 Use of theory and model systems

6.1.1 General considerations

In this thesis the adsorption of polyelectrolytes on oppositely charged surfaces is investigated, both theoretically and experimentally. From the theory (chapter 2) it emerged that two regimes can be distinguished in polyelectrolyte adsorption, the *screening-enhanced adsorption* regime and the *screening-reduced adsorption* regime. In the former regime the adsorption increases with increasing salt concentration due to screening of the repulsion between the segments and a nonelectrostatic interaction between polyelectrolyte and surface, whereas in the latter the adsorption decreases with increasing salt concentration because the, mainly electrostatic, attraction between polyelectrolyte and surface is screened. A transition from one regime to the other is also possible. The existence of the two regimes explains seemingly contradicting experimental results. In most investigations (for instance in the PhD-theses of van der Schee [1] and Bonekamp [2]) the adsorption of polyelectrolytes was found to increase with increasing salt concentration, whereas others found (for instance [3, 4, 5]) monotonously decreasing adsorption. The theory explains that the ionic strength, the surface charge density, the segment charge and the strength of the nonelectrostatic interaction are the most important variables in polyelectrolyte adsorption. If salt ions have a nonelectrostatic interaction with the surface, a maximum in the adsorbed amount can occur provided the nonelectrostatic interaction of the polyelectrolyte with the surface is large enough.

The experimental system in this thesis, cationic starch adsorbing on microcrystalline cellulose, is not such a nice model system as, for instance, polylysine adsorbing on AgI-particles [1], but its behaviour is obviously dominated by the presence of charges and this can be explained very well with the theory in chapter 2. The adsorption of cationic amylopectin from waxy maize showed a maximum as a function of the salt concentration (chapter 4) and we were able to explain this with our theory. We also verified that salt cations had specific interactions with the cellulose surface, as predicted by the theory. We found that, if the adsorption decreased with increasing salt concentration, it was sensitive to the type of salt cation and that the adsorption in the presence of alkali cations decreased in the order $Li^+ > Na^+ \approx K^+ > Cs^+$. The adsorption of cationic potato starch monotonously decreased with increasing salt concentration, but from the experiments it was unclear whether or not a

sensitivity to the type of salt as for cationic amylopectin exists (chapter 5).

6.1.2 Relevance for papermaking

Although it is not common practice in papermaking research to make use of model systems and theories, the results in this thesis show that they can be very helpful in understanding what is happening.

Often experiments are carried out with systems still very close to the real papermaking system. The presence of many components, commercial samples that are unpure or polydisperse, and an unsystematic approach, make the experiments valid only under certain circumstances, which are sometimes not properly described either. There is no doubt about the usefulness of such experiments, but the chance is large that we stay, as was stated by Cushing and Schuman [6], " surrounded by the darkness of lack of detailed knowledge of the real nature of the products we use and the absence of a mechanism to explain how they produce the results we obtain." And "we are, then, like the seven blind men attempting to define an elephant–it all depends where we touch the beast." Therefore, the experiments described in this thesis were carried out with as few components as possible, and these components were characterised as well as possible. If complete characterisation was beyond our possibilities, as was the case for starch, the relevant literature was studied carefully. This approach helped us to find the preferential adsorption of amylose from potato starch, and to explain it. A theory helps to find the relevant variables for experiments and to explain the experimental results in general terms. Polyelectrolyte adsorption theory revealed that relevant variables in adsorption studies are surface charge density, polyelectrolyte charge density and salt concentration. It also helped to assess what seemingly different systems have in common. In this way, it was easier to recognize the similarities between adsorption of cationic starch and various synthetic polyelectrolytes on cellulose. The fact that it is quite well possible to explain our experimental results in terms of a theory dealing with ideal polyelectrolytes and ideal surfaces (chapter 4 and 5) emphasizes that it is not necessary to attribute these results to special properties of starch or cellulose.

In our experiments we used microcrystalline cellulose as a model for cellulose fibers. From the electron micrographs in chapter 3, it is clear that our microcrystalline cellulose is level-off DP cellulose, which means that microcrystalline cellulose differs from cellulose fibers with respect to the length of the cellulose polymers (smaller in microcrystalline cellulose, level-off DP) and the amount of crystalline regions (larger in

microcrystalline cellulose). Another important difference is that cellulose fibers usually have higher surface charges, as measured by potentiometric titrations, than our microcrystalline cellulose (-1.2 C/g at pH=7). At pH=7bleached fibers of different origin have surface charges between -3 and -6.6 C/g, whereas unbleached fibers have surface charges of about -9 C/g [7, 8]. Budd and Herrington [8] give for the surface charge densities values between -0.04 and -0.08 C/m^2 both for bleached and unbleached fibers. If the larger surface charge density is the main difference between cellulose fibers and microcrystalline cellulose, we expect for the former a larger adsorbed amount of cationic starch. Our values for the adsorption of a quaternary cationic potato starch on microcrystalline cellulose without added salt, 16 mg/g for DS=0.035 or σ_{ads}=3.5 meq/g, are indeed lower than those reported in literature for cellulose fibers (see table 1 of chapter 5). Marton and Marton found 15 mg/g for cationic starch with DS=0.054 or σ_{ads}=5 meq/g [9] and Krogerus 35 mg/g for a cationic starch with DS=0.025 or σ_{ads}=5.4 meq/g [10], both measured without added salt. Since the adsorbed amount varies linearly with the surface charge (chapter 2, 4 and 5), this indicates that the surface charge of the cellulose fibers used by Marton and Marton and Krogerus, is 1.4 to 1.6 times larger than that of microcrystalline cellulose. This is in the right order of magnitude as found by Budd and Herrington, so we can conclude that the main difference between microcrystalline cellulose and cellulose fibers is the surface charge density. Therefore, the results given in this thesis for microcrystalline cellulose, are also valid for cellulose fibers if the difference in surface charge density is taken into account.

The results described in this thesis, were obtained under relatively static conditions as compared to the very dynamic process of papermaking. However, since the electrostatic interaction between cationic starch and cellulose is the most important parameter, we expect that the trends from our static experiments to be also valid for a more dynamic system. Of course this has to be checked in dynamic experiments, for which the results in this thesis can form the starting point.

6.2 Cationic starch as a polyelectrolyte

We have shown (chapters 4 and 5) that the adsorption behaviour of cationic starch is to a large extent determined by its polyelectrolyte character, which is indicated by the pronounced influence of salt concentration and pH. This means that we can predict, with a reasonable degree of success, its behaviour for circumstances we did not investigate

yet, based on our knowledge of polyelectrolyte adsorption in general (chapter 2) and of polyelectrolyte adsorption on cellulose in particular. A good review of the latter is given by Lindström [11]. The early investigations of Trout [12] in 1951, showing that the adsorption of polyethylenimine on cellulose is mainly driven by electrostatic attraction, had a large influence on later research concerning the adsorption of synthetic polyelectrolytes on cellulose. It is very surprising that this hardly affected the work done on cationic starch in the 1960's and that Marton and Marton [9] in 1976 were the first to show the importance of the electrostatic attraction for the adsorption of cationic starch on cellulose.

In the literature about polyelectrolyte adsorption on cellulose, and also at conferences, for example at the Fundamental Research Symposium in 1989 [13], it is often discussed whether the main driving force for adsorption is the accessible surface area, the charge interaction or nonelectrostatic interactions. The theory on polyelectrolyte adsorption helps us to find an answer to this question as far as the relative importance of the electrostatic and nonelectrostatic interactions is concerned. Before dealing with this in more detail, we like to point out that experiments as reported in literature were often carried out in demineralized water, so the salt concentration is very low. According to the theory, the electrostatic interaction dominates at very low salt concentration, causing the polyelectrolyte to adsorb to such an extent as so compensate the (available) surface charge. At higher salt concentration, however, nonelectrostatic interactions between polymer and surface start playing a role. Therefore, to establish the importance of the nonelectrostatic interactions, the influence of a range of salt concentrations on the adsorption of the polyelectrolyte must be known. The adsorbed amount will drop with increasing salt concentration (*screening reduced adsorption* regime), if the electrostatic interaction is the main driving force for adsorption. The variables which at a given ionic strength determine the strength of the electrostatic interaction, are the surface charge density and the charge density of the polyelectrolyte. On the other hand, if the adsorption increases with increasing salt concentration (*screening enhanced adsorption* regime) the nonelectrostatic, short-range, attraction between polymer and surface is the most important contribution. The resulting salt effect of course depends on the balance between the electrostatic and nonelectrostatic interaction, but this applies to most cases. The adsorption of polyethylenimine, cationic polyacrylamides, and polyDMDAAC (dimethyldiallylammonium chloride) on cellulose was found to decrease

with increasing salt concentration, [14, 15, 16], [17-22] and [19] respectively, so the electrostatic interaction is the driving force for adsorption. The theory predicts that for polyelectrolytes with a very low charge density (less than 10% charged segments) the *screening-reduced adsorption* regime occurs nearly exclusively, irrespective of the strength of the nonelectrostatic interaction, provided the (absolute) surface charge density is not too low (≥0.02 C/m^2). This condition applies to cationic starch and to low charged cationic polyacrylamides because the (absolute) surface charge density on cellulose fibers is larger than 0.02 C/m^2 [7, 8]. Indeed it is found that the adsorption of these polyelectrolytes decreases with increasing salt concentration (chapter 4 and 5 and [17, 23]). Thus, the electrostatic interaction is always the main driving force for adsorption of these low charged polyelectrolytes on cellulose. This dominance of the electrostatic interaction causes an interesting effect, namely a maximum in the adsorbed amount as a function of the polyelectrolyte charge density (degree of substitution). Regardless the strength of the nonelectrostatic interaction with the surface the affinity for the negatively charged surface is greatly enhanced by introducing a few cationic charges in a polymer. If the charge density becomes higher than that at the maximum (about 1% of the segments is charged), the adsorbed amount decreases with increasing charge density, because the ability of the polymer to recharge the surface is also increased. As soon as the surface has become positive, further adsorption of the polymer is limited by electrostatic repulsion between polymer and surface. Such a maximum in the adsorbed amount as a function of the DS was found for the adsorption of cationic polyacrylamides on cellulose [11, 17] and for cationic starch [24].

The theory does not account for differences in accessible surface area for polyelectrolytes with different molecular weigths, such as those due to porosity of the cellulose fibers. From experimental results reported in literature (for instance [25, 26]) it is clear that polyelectrolytes with molecular weigth between 5,000 and 10,000 are able to enter most pores, whereas larger polyelectrolytes tend to "see" only 10% of the total surface (charge). The adsorbed amounts of small and large polyelectrolytes can therefore be very different. The polydispersity of many commercial samples probably complicates the understanding of their adsorption behaviour [25]. Other properties of the polyelectrolytes under investigation, like size and shape in solution or tendency to form complexes, might of course also affect the adsorption.

Considerations on (polymer) adsorption from solution in general, might throw some light on the fact that the nonelectrostatic interaction of

polyelectrolytes with the cellulose surface is usually weak. If a polymer segment adsorbs from aqueous solution, it has to displace water molecules from the surface. Therefore, the adsorption energy of a polymer segment χ_s (in units kT) is the difference between the interaction of the polymer segment with the surface, χ_P, and that of the water molecules, χ_w. Since cellulose is very hydrophilic, χ_w will be rather large. To end up with a χ_s large enough to make the polymer adsorb, χ_P must be larger than χ_w. Hence, the net nonelectrostatic interaction of the polymer with cellulose χ_s, might be small in general, because water has a strong interaction with the cellulose surface.

6.3 Comparison of the adsorption behaviour of cationic waxy maize and cationic potato starch

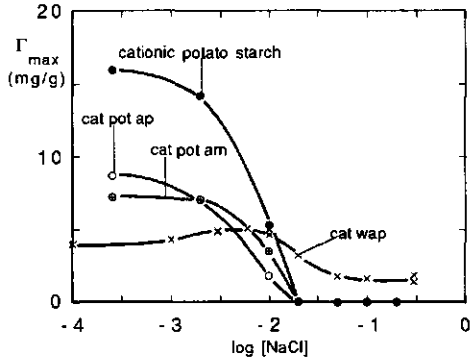

Figure 1. The influence of [NaCl] on the plateau value of the adsorption of cationic potato starch (● total carbohydrate; ⊕ cat pot am, cationic amylose from potato starch; o cat pot ap, cationic amylopectin from potato starch; DS=0.035) and cationic waxy maize (x-x, cat wap, DS=0.035) on microcrystalline cellulose, 40 g/l cellulose, pH in both cases 6-7.

The adsorption of cationic potato starch and cationic amylopectin from waxy maize on microcrystalline cellulose (figure 1) differs in three respects. Firstly, the adsorption of cationic potato starch decreases monotonously with increasing salt concentration, whereas the adsorption of cationic amylopectin shows a maximum as a function of the salt concentration. Secondly, the adsorbed amount of cationic potato amylopectin is about twice that of cationic waxy maize amylopectin for [NaCl]<0.01 M. Thirdly, the adsorption of cationic potato starch decreases to zero, whereas a small amount of cationic waxy maize stays adsorbed even at high salt concentration. The last difference may be only

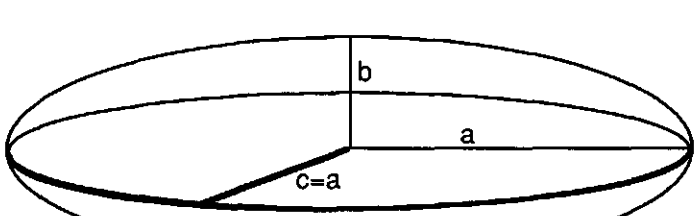

Figure 2. Oblate ellipsoid of rotation. The axes a and c are the longest and equal to each other. Axis b is the shortest axis.

an apparent one, since the experimental error for [NaCl]>0.01 M in the curve for catinioc potato starch is so large that it was not possible to distinguish between a small adsorbed amount and nothing adsorbed at all (see also appendix A.2). The explanation for the other two differences in adsorption might be found in different molecular shapes and different molecular weights of the two amylopectins. Callaghan et al. [27] concluded from NMR diffusion measurements that wheat and potato amylopectin in water have the shape of an oblate ellipsoid (pancake, figure 2). Such a shape for amylopectin was also suggested by Banks and Greenwood [28, 29], based on the synthesis of amylopectin as a two-dimensional entity and the hydrodynamic behaviour of amylopectin. Callaghan et al. found that the size and shape of wheat amylopectin in water were different from those in DMSO. The oblate elipsoid was flatter in DMSO than in water, with ratios between the long (a=c) and the short axis (b) respectively 17.5 and 8. The volume of wheat amylopectin in water was 400 times larger than that in DMSO, which led Callaghan et al. to the conclusion that wheat amylopectin forms complexes in water with molecular weights of the order of 10^8, whereas it occurs as free molecules in the much better solvent DMSO with molecular weights of about 10^6. The shape of potato amylopectin in water is between these two, with a/b=12 [30]. Callaghan et al. suggested that aggregation of potato amylopectin is inhibited by the presence of charged phosphate groups. Therefore, we will assume that cationic amylopectin does not form complexes. Of course, we need information on waxy maize amylopectin instead of wheat amylopectin. Since it is well known that properties of starches are closely related to their botanical source, and that starches from cereals share several properties, as do starches from tubers [29, 31], it seems justified to assume that amylopectin from cationic waxy maize has approximately the same shape as wheat

amylopectin in DMSO. If amylopectin adsorbs with its flattest side (the longest axes, *a* and *c*, parallell to the surface) on the cellulose surface, the adsorbed amount of potato amylopectin, occupying the same surface area, will be 1.5 times larger, either because potato amylopectin is thicker (*b* is larger) if *a* is the same as of waxy maize amylopectin, or because both *a* and *b* of potato amylopectin are smaller so more molecules can be packed on the same area. The latter could also explain why cationic potato amylopectin is desorbed more easily with increasing salt concentration. The contact area of the "spherical" potato amylopectin is smaller than that of waxy maize amylopectin, so the electrostatic interaction with the surface is more easily screened. Waxy maize amylopectin, on the other hand, has a larger contact area (*a* is larger, as we mentioned before), which becomes smaller with increasing salt concentration, because the molecule then collapses upon itself, giving a spheroid, due to screening of the repulsion between the cationic groups in the molecule. This leads to an increased layer thickness, and therefore to an increase in the adsorbed amount. At yet higher salt concentration, the electrostatic interaction between cationic waxy maize amylopectin and the surface is also screened and the adsorbed amount decreases. Moreover, a molecule of cationic potato amylopectin might be larger, since the sedimentation coefficient (chapter 3) of waxy maize is about 150 S while that of potato amylopectin is 210 S, indicating that the molecular weight of waxy maize is approximately $4 \cdot 10^7$ and that of potato amylopectin $25 \cdot 10^7$. This could also explain the much higher level of adsorption reached in 2 mM NaCl by cationic amylopectin obtained from cationic potato starch by ultracentrifugation, in the absence of competing amylose molecules (16 mg/g, chapter 5).

Although the preceeding considerations are rather speculative, it seems reasonable to assume that the different adsorption behaviour of cationic waxy maize amylopectin and cationic potato amylopectin is caused by differences in molecular shape and molecular weight. From the small difference in effect between Ca^{2+} and Mg^{2+} on the adsorption of cationic potato starch (section 5.3.4.2) we concluded that the occurence of phosphate groups in potato amylopectin plays no relevant role in this.

6.4 Some results with direct relevance for papermaking

6.4.1 Retention

Our results on the adsorption of cationic potato starch and cationic waxy maize show that if about 1.5% (on dry fiber weight) is added, the retention at low salt concentration (2 mM NaCl) and pH≈7) is almost

100% for cationic potato starch, but only 50% for cationic waxy maize. If the retention of cationic potato starch is 100%, the preferential adsorption of amylose does not show of course. The better retention of potato starch is caused by the presence of amylose, since the retention of cationic amylopectin from potato starch is almost the same as that of cationic amylopectin from waxy maize. However, the retention of cationic potato starch drops to 50% if the salt concentration is increased to 0.01 M NaCl, whereas that of cationic waxy maize hardly changes. At still higher salt concentration, the retention of both cationic starches reduces to about 10% or even zero. This means that simple monovalent salts can be detrimental substances. The effect of divalent cations, such as Ca^{2+}-ions, is ten times larger, so they can be detrimental substances at even lower concentrations. We have also shown, by theory (chapter 2) and by experiment (chapter 5), that the detrimental influence of high salt concentrations is least for cationic starch with the highest DS. So recommendations by starch manufacturers to use cationic starches with high DS in papermaking systems with high conductivity (= high salt concentration) indeed make sense.

6.4.2 Retention of cationic starch versus cationic starch as a retention aid

To understand the effect of salt concentration on the performance of cationic starch, it is necessary to discriminate between the adsorption (retention) of cationic starch and cationic starch as a retention aid for fines and fillers. We have pointed out above, that as far as the adsorption of cationic starch is concerned, simple salts can be important detrimental substances. However, such a detrimental effect of salts is not found if cationic starch is used as a retention aid [32]. The explanation is found in the conformation change of the polyelectrolytes with increasing salt concentration. In chapter 4, it is shown how polyelectrolytes are displaced from the surface by salt ions. As the concentration of displacer increases, more and longer loops and longer tails are formed. Just before complete displacement, the polyelectrolyte might be attached to the surface by only one segment, but even then it is able to form a bridge between two particles to flocculate them. So polyelectrolytes can act as flocculating agents as long as they can become attached to the surfaces they are meant to flocculate.

Davison [32] also compared the flocculation efficiency of cationic starch with that of cationic polyacrylamide, and found that the latter was more effective. This can be understood by the differences of conformation in solution between these polyelectrolytes. Cationic polyacrylamide is a low

charged, linear polyelectrolyte, and if adsorbed on a surface, it can have long loops and tails sticking out in solution to promote flocculation. Cationic starch on the other hand, consists for about 80% of amylopectin, which might have the conformation of a pancake in solution [27], so it is less effective in promoting flocculation.

6.4.3 Cationic starch as a dry strength agent

As we have seen in chapter 2, the adsorption of very low charged polyelectrolytes can be very high, since the introduction of a few charges strongly promotes the adsorption. Therefore, cationic starches with a low DS can be used if it is desired to make papers containing large amounts of starch, for instance in filled papers [33, 34]. A similar conclusion, based on experiments, was reached by Stoutjesdijk and Smit [35].

Although the retention of cationic potato starch at low salt concentration is considerably higher than that of cationic waxy maize, this does not necessarily mean that paper dry strength is improved more by cationic potato starch. The higher retention of cationic potato starch is related both to the presence of amylose and to the size, shape and molecular weight of amylopectin. Since it was found by several investigators that native amylopectin improves dry strength more than amylose [36, 37, 38], it would be interesting to know whether the same holds for the cationic derivatives. If that is indeed the case, it may be more effective to use cationic waxy maize instead of cationic potato starch to obtain the desired dry strength. To papermakers, therefore, comparison between the dry strengths gained by the addition of cationic potato starch and cationic waxy maize can be of importance.

6.5 References

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APPENDIX 1 ADSORPTION OF CATIONIC WAXY MAIZE

A1.1 Adsorption isotherm

Table A1.1. Adsorption isotherm of cationic waxy maize on microcrystalline cellulose, 40g/l cellulose, 0.01 M NaCl, pH=5.8, corresponding to figure 1 in chapter 4.

c_{eq} (mg/l)	Γ (mg/g)	$c_{eq,c}$ (mg/l)	Γ_c (mg/g)
8.4	4.7	8.4	4.7
380.3	5.5	391	5.2
787.6	5.3	802.7	4.9
1597.0	5.	1611.1	4.6
2308.2	4.7	2318.9	4.5

c_{eq} : equilibrium concentration
$c_{eq,c}$: equilibrium concentration corrected for cationic waxy maize that was centrifuged off (see 3.4.2)
Γ_c : adsorbed amount corrected for cationic waxy maize that was centrifuged off (see 3.4.2)

A1.2 Plateauvalues

Table A1.2. Plateauvalues of cationic waxy maize as a function of [NaCl], corresponding to figure 2 of chapter 4.

[NaCl] (M)	c_{eq} (mg/l)	Γ (mg/g)	$c_{eq,c}$ (mg/l)	Γ_c (mg/g)
0.0001	833.8	4.1	838.5	4.0
0.0001	823.5	4.1	826.5	4.0
0.001	820.6	4.5	827.2	4.3
0.003	782.5	5.5	786.4	5.0
0.003	791.7	5.1	803.1	4.9
0.006	773.8	5.3	782.9	5.1
0.01	779.4	5.5	798.5	5.1
0.01	778.3	5.2	799.5	4.7
0.02	848.8	3.7	870.6	3.2
0.05	897.0	2.6	929.9	1.8
0.1	420.2	2.0	436.4	1.6
0.3	431.0	1.9	450.7	1.4
0.3	419.8	2	425.1	1.8

Table A.1.3a. Plateau values of cationic waxy maize as a function of [NaCl] and pH, corresponding to figure 4 in chapter 4.

pH 0.001 M	$-\sigma_0$ (C/g) 0.001 M	Γ_c (mg/g) 0.001 M	σ_{ads} (C/g) 0.001 M	pH 0.01 M	$-\sigma_0$ (C/g) 0.01 M	Γ_c (mg/g) 0.001 M	σ_{ads} (C/g) 0.01 M
3.2	0	2.0	0.044	3.0	0	1.3	0.027
3.9	0.015	2.8	0.060	3.9	0.067	3.3	0.071
5.0	0.54	3.8	0.083	4.7	0.50	4.6	0.099
5.9	0.88	4.2	0.091	5.9	0.91	5.3	0.115
7.0	1.04	4.5	0.098	6.6	1.00	5.4	0.116
7.7	1.08	4.9	0.106	7.2	1.08	5.6	0.120
9.0	1.35	4.9	0.106	7.9	1.13	5.9	0.127
9.7	1.75	5.2	0.113	8.9	1.37	6.2	0.134

σ_0 charge on the *bare* surface, obtained from the potentiometric titrations in chapter 3.1.6

σ_{ads} calculated by $\Gamma_c \cdot 0.035 \cdot F/162$, where F is Faraday's constant, 162 the molecular weight of a glucose unit and 0.035 the DS of cationic waxy maize.

Table A.1.3b. Plateau values of cationic waxy maize as a function of [NaCl] and pH, corresponding to figure 4 in chapter 4.

pH 0.03 M	$-\sigma_0$ (C/g) 0.03 M	Γ_c (mg/g) 0.03 M	σ_{ads} (C/g) 0.03 M	pH 0.1 M	$-\sigma_0$ (C/g) 0.1 M	Γ_c (mg/g) 0.1 M	σ_{ads} (C/g) 0.1 M
3.1	0	0.8	0.030	3.1	0	1.1	0.037
3.8	0.17	1.4	0.040	3.8	0.32	1.7	0.035
5.3	0.83	1.8	0.052	5.2	0.90	1.6	0.037
10.2	1.90	2.4	0.051	6.0	1.00	1.7	0.035
6.6	1.05	2.4	0.049	6.7	1.05	1.6	0.022
6.2	1.00	2.3	0.058	9.9	1.83	1.0	0.023
10.4	2.00	2.7	0.072	10.6	2.00	1.1	0.031
11.0		3.3		11.1		1.4	

σ_0 charge on the *bare* surface, obtained from the potentiometric titrations in chapter 3.1.6

σ_{ads} calculated by $\Gamma_c \cdot 0.035 \cdot F/162$, where F is Faraday's constant, 162 the molecular weight of a glucose unit and 0.035 the DS of cationic waxy maize.

APPENDIX 2 ADSORPTION OF CATIONIC POTATO STARCH

In the following tables, the values corresponding to the adsorption isotherms in the figures of chapter 5 are given. Γ_{starch} is the adsorbed amount of total carbohydrate, as determined with the sulphuric acid-phenol method (section 3.3.1). Γ_{am}, the adsorbed amount of amylose, and Γ_{ap}, the adsorbed amount of amylopectin, are calculated as described in section 3.4.3. The equilibrium concentrations of starch (st, total carbohydrate), amylose and amylopectin are given. The part of the adsorbed amount which is amylose or amylopectin (% am/ap of Γ_{starch}), is also given.

Table A2.1. Adsorption of cationic potato starch (DS=0.035) (Z), amylose-rich (AM) and amylopectin-rich fraction obtained from cationic potato starch by ultracentrifugation, on *untreated* microcrystalline cellulose. 2 mM NaCl, 40 g/l cellulose, pH=6.5. Values corresponding to figures 1-4 from chapter 5.

Z, 21% amylose in initial solution							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
0.0	0.0	0.0	6.3	1.3	5.0	21	79
239.4	21.8	217.6	9.0	2.6	6.4	28.9	71.2
634.9	78.3	556.6	11.6	3.8	7.8	32.8	67.2
1231.4	200.4	1031.0	14.2	4.4	9.8	31.2	68.2
1790.4	320.0	1470.4	17.7	5.1	12.6	28.9	71.1
AM, 67.5% amylose in initial solution							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
0.0	0.0	0.0	2.0	1.3	0.6	67.5	32.5
12.9	8.4	4.5	4.4	3.0	1.4	67.7	32.3
35.0	17.5	17.5	7.7	5.4	2.4	69.5	30.5
63.6	33.9	29.7	12.5	8.6	3.8	69.3	30.7
99.7	59.1	40.6	16.9	11.6	5.3	68.7	31.3
AP, 3% amylose in initial solution							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
0.0	0.0	0.0	5.8	0.2	5.6	3	97
163.9	6.7	157.2	9.8	0.3	9.6	2.5	97.5
479.0	20.9	458.2	13.5	0.2	13.3	1.8	98.2
912.7	50.7	862.0	18.9	0.0	18.9	-	100
1408.2	81.9	1326.3	22.8	0.0	23.1	-	100

Table A2.2. Influence of the cellulose concentration on the adsorption of cationic potato starch (DS=0.035) on cleaned microcrystalline cellulose. Values corresponding to figure 5 of chapter 5. 2 mM NaCl, pH=6. The nonadsorbed amount Γ^* is calculated from $c_e/c_{cellulose}$, where c_e is the equilibrium concentration of starch, amylose or amylopectin, and $c_{cellulose}$ is the cellulose concentration (either 5 g/l or 40 g/l).

5 g/l cellulose										
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{sta}	% ap of Γ_{sta}	Γ^*_{sta} (mg/g)	Γ^*_{am} (mg/g)	Γ^*_{ap} (mg/g)
4.3	0.0	4.4	5.1	1.3	3.8	24.8	75.2	0.9	0.0	0.9
35.5	2.7	32.8	7.8	2.6	5.2	33.2	66.8	7.1	0.5	6.6
81.2	9.8	71.4	11.7	3.9	7.8	33.5	66.5	16.2	1.9	14.3
154.7	22.0	132.8	13.8	5.0	8.8	36.4	63.6	31.2	4.4	26.8
237.2	35.2	202.0	14.8	6.0	8.8	40.6	59.4	46.8	6.9	39.9
40 g/l cellulose										
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{sta}	% ap of Γ_{sta}	Γ^*_{sta} (mg/g)	Γ^*_{am} (mg/g)	Γ^*_{ap} (mg/g)
12.0	0.0	12.3	6.0	1.3	4.6	22.6	77.8	0.3	0.0	0.3
260.0	15.9	244.1	8.5	2.7	5.7	32.4	67.6	6.5	0.4	6.1
687.1	60.3	626.8	10.3	4.3	6.1	41.4	58.6	17.2	1.5	15.7
1301.8	169.6	1132.2	12.4	5.2	7.2	41.8	58.2	32.5	4.2	28.3
1987.4	281.5	1705.9	12.8	6.1	6.7	47.5	52.5	49.6	7.0	42.6

Table A2.3a. The influence of the electrolyte concentration on the adsorption of cationic potato starch (DS=0.035) on cleaned microcrystalline cellulose. 40 g/l cellulose, 2 mM NaCl, pH=6.5. Values corresponding to figure 6 of chapter 5. Other values for 2 mM NaCl are taken from table A.2.2.

$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
0.0	0.0	0.0	6.1	1.3	4.8	21	79
220.1	12.1	208.0	9.4	2.8	6.6	30	70
644.0	44.6	599.4	11.4	4.7	6.8	40.8	59.2
1305.5	123.7	1181.8	12.3	6.3	6.0	51.5	48.5
1963.0	234.9	1728.1	13.4	7.2	6.1	54.1	45.9

Table A2.3b. The influence of the electrolyte concentration on the adsorption of cationic potato starch (DS=0.035) on cleaned microcrystalline cellulose, 0.01 M NaCl, pH≈7, 40 g/l cellulose. Values corresponding to figure 6 of chapter 5.

pH=6.5							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
47.8	11.9	35.9	5.0	1.0	4.0	20.1	79.9
384.3	56.2	328.1	5.4	1.7	3.6	32.4	67.7
871.4	152.7	718.6	5.7	2.0	3.8	34.2	65.8
1602.7	289.8	1312.9	4.9	2.2	2.7	44.6	55.4
2324.8	434.2	1890.7	4.4	2.3	2.1	51.7	48.3
pH=7							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
8.7	1.2	7.5	4.8	1.0	3.8	21.3	78.7
173.9	2.7	171.2	5.6	2.0	3.6	35.9	64
541.9	102.1	439.8	6.4	1.6	4.8	25.5	74.5
948.9	190.8	758.1	6.3	1.5	4.8	24.4	75.6
1334.2	261.4	1072.8	6.8	1.9	4.9	28	72
1701.5	349.1	1352.4	6.3	1.5	4.8	24.3	75.7

Table A2.4. Plateauvalues of the adsorption of cationic potato starch (DS=0.035) on cleaned microcrystalline cellulose, as a function of [NaCl], pH varied from 7.6 for the lowest [NaCl] to 5.7 for the highest [NaCl], 40 g/l cellulose, initial concentration≈2500 mg/l. Values corresponding to figure 7 of chapter 5.

[NaCl] (M)	$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	%am of Γ_{starch}
0.00025	1859.9	234.9	1625	16.0	7.2	8.7	45.4
0.002	1930.2	241.7	1688.5	14.2	7.1	7.1	49.8
0.01	2284.9	383.6	1901.3	5.3	3.5	1.8	66.2
0.02	2514.8	468.23	2046.5	–0.34	1.422	–1.77	–
0.05	2581.3	484.0	2097.3	–1.98	1.032	–3.01	–
0.1	2542.0	507	2028.1	–1.11	0.403	–1.51	–
0.2	2596.3	523.7	2072.6	–1.97	0.121	–2.09	–

TableA.2.5. The plateau values of cationic potato starch (DS=0.035) adsorbing on cleaned microcrystalline cellulose, pH=5, 40 g/l cellulose, the electrolyte concentration was 0.01 M, initial concentration≈600 mg/l. Values corresponding to table 3 of chapter 5.

type of salt	$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	%am of Γ_{starch}
NaCl	474.6	85.5	389.0	3.1	1.0	2.1	32.2
NaCl	468.1	84.6	383.5	3.3	1.0	2.3	31.3
NaCl	469.6	85.0	384.6	3.3	1.0	2.3	31.3
KCl	460.4	93.3	367.1	3.4	0.8	2.6	23.4
KCl	453.8	94.0	359.8	3.6	0.8	2.8	21.9
KCl	469.7	94.0	375.6	3.2	0.8	2.4	24.6
CsCl	474.7	98.9	375.8	3.1	0.7	2.4	21.6
CsCl	462.4	99.4	363	3.4	0.7	2.7	19.4
CsCl	468.1	97.6	370.6	3.2	0.7	2.5	21.4

Table A2.6. The effect of type of electrolyte on the adsorption of cationic potato starch (DS=0.035) on cleaned microcrystalline cellulose, pH=5, 40 g/l cellulose. Values corresponding to figure 8 in chapter 5. The values for 0.01 M NaCl, pH=5 are taken from table A.2.8.

0.01 M CsCl							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
88.0	16.3	71.4	2.8	0.6	2.2	22.8	77.2
304.6	50.5	254.1	2.4	0.8	1.6	35.0	65.0
469.8	85.1	384.7	2.5	0.9	1.6	35.7	64.4
975.8	196.4	779.4	3.1	0.9	2.3	27.8	72.3
1655.4	316.7	1338.7	1.1	1.1	0.0	94.0	6.0
2488.5	466.3	2022.2	0.3	1.5	-1.2	-	-

Table A2.7. The effect of divalent cations on the adsorption of cationic potato starch (DS=0.035) on cleaned microcrystalline cellulose, 40 g/l cellulose, pH=5. Values corresponding to figure 9 in chapter 5.

1 mM $CaCl_2$							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
7.7	0.0	7.9	3.9	0.9	3.0	22.1	77.9
130.1	11.2	118.9	4.9	1.4	3.5	29.2	70.8
453.2	64.6	388.6	5.1	1.8	3.2	36.1	63.9
787.8	132.4	655.4	4.9	1.9	3.1	37.8	62.2
1133.3	205.3	928.0	4.4	1.7	2.7	39.3	60.7
1450.5	268.4	1182.2	4.7	1.9	2.8	40	60
1 mM $MgCl_2$							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	%ap of Γ_{starch}
4.1	0.0	4.2	4.0	0.9	3.2	21.6	78.4
121.8	9.9	111.9	5.1	1.5	3.7	28.5	71.5
415.0	58.6	356.4	6.0	2.0	4.0	32.9	67.1
762.8	119.2	643.6	5.5	2.2	3.3	39.5	60.5
1083.7	190.1	893.5	5.8	2.2	3.6	37.2	62.8
1419.6	248.7	1170.9	5.5	2.4	3.1	43.3	56.7

Table A2.8. The effect of pH on the adsorption of cationic potato starch (DS=0.035) on cleaned microcrystalline cellulose, 40 g/l cellulose. Values for pH=7 and pH=6.5 are taken from table A2.3b. Values corresponding to figure 10.

10 mM NaCl, pH=5							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
44.3	10.3	34.0	3.8	0.8	3.0	20.3	79.7
233.1	5.2	227.9	3.9	2.0	1.9	50.7	49.3
642.5	123.0	519.5	4.0	1.1	2.8	28.5	71.5
958.1	217.8	740.3	6.0	0.8	5.1	14	86
1360.5	281.4	1079.0	5.9	1.4	4.6	22.8	77.2
1863.6	375.5	1488.1	3.4	1.1	2.3	32.7	67.4
10 mM HCl, pH=2							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
221.9	42.7	179.2	0.7	0.2	0.5	34.9	65.1
573.5	110.9	462.6	0.6	0.4	0.2	60.4	39.6
1049.2	218.0	831.2	0.7	0.2	0.5	29.1	70.9
1471.1	372.9	1098.2	5.8	-0.5	6.3	-	-
2383.2	513.4	1869.8	2.9	0.3	2.6	10	90

Table A2.9. The effect of DS on the adsorption of cationic potato starch on cleaned microcrystalline cellulose, 40 g/l cellulose, 2 mM NaCl, pH=5. Values corresponding to figure 11 of chapter 5.

DS=0.017							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
13.8	0.0	15.0	4.7	1.1	3.6	23.2	76.8
84.5	3.6	80.9	7.8	2.0	5.8	25.5	74.5
423.6	48.4	375.2	9.3	3.0	6.3	32	68
820.9	114.5	706.4	9.5	3.4	6.0	36.3	63.7
1193.1	190.5	1002.6	10.1	3.6	6.5	35.8	64.2
1638.9	261.0	1377.9	9.0	4.0	5.1	44	56
DS=0.047							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
13.4	1.1	12.3	4.7	1.0	3.6	21.9	78.1
171.5	15.3	156.2	5.7	1.7	4.0	30	69.9
497.0	63.5	433.5	7.6	2.6	5.0	34.4	65.6
903.2	127.9	775.3	7.4	3.1	4.3	41.9	58.1
1283.5	211.7	1071.8	8.0	3.1	4.9	39.1	60.9
1649.1	284.5	1364.7	8.8	3.4	5.4	38.5	61.5

Table A2.10. The effect of DS on the adsorption of cationic potato starch on cleaned microcrystalline cellulose, 40 g/l cellulose, 0.01 M NaCl, pH=5. Values corresponding to figure 12 in chapter 5. Values for DS=0.035 are taken from table A2.8.

DS=0.017							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
89.5	14.9	74.5	2.8	0.7	2.1	24.5	75.5
273.5	50.2	223.4	3.2	0.9	2.3	26.7	73.3
666.3	122.9	543.3	3.4	1.1	2.2	33.7	66.3
1076.7	202.6	874.1	3.1	1.2	1.9	39.8	60.2
1451.3	290.1	1161.3	3.7	1.1	2.6	30.9	69.1
1866.4	364.8	1501.6	3.3	1.4	2.0	41.3	58.7
DS=0.047							
$c_{e,st}$ (mg/l)	$c_{e,am}$ (mg/l)	$c_{e,ap}$ (mg/l)	Γ_{starch} (mg/g)	Γ_{am} (mg/g)	Γ_{ap} (mg/g)	% am of Γ_{starch}	% ap of Γ_{starch}
45.9	7.2	38.7	3.8	0.9	3.0	22.6	77.38
226.5	37.2	189.3	4.1	1.1	3.0	27.5	72.55
653.1	116.3	536.8	3.7	1.3	2.4	35.1	64.9
992.4	185.0	807.4	3.5	1.4	2.1	38.8	61.17
1475.7	284.1	1191.6	3.1	1.3	1.8	42.1	57.9
1737.6	366.2	1371.5	6.6	1.3	5.2	20.5	79.5

SUMMARY

Cationic starches are used on a large scale in paper industry as wet-end additives. They improve dry strength, retention of fines and fillers, and drainage. Closure of the white water systems in the paper mills hase increased the concentration of detrimental substances. This might be the reason for the poor retention of cationic starches observed in the last few years.

The purpose of the research described in this thesis was to obtain a better understanding of the adsorption of cationic starch on cellulose and how this interaction can be disturbed. In contrast to most research in papermaking we have used a colloid-chemical approach. This means that we kept our experimental system as simple as possible and therefore far from the reality of papermaking.

In chapter 2 we tried to generalize the specific problem of cationic starch adsorption on cellulose to polyelectrolyte adsorption on an oppositely charged surface. We used a recent extension of the polymer adsorption theory of Scheutjens and Fleer for polyelectrolyte adsorption to perform model calculations. It emerged that, for the adsorption of a strong polyelectrolyte on an oppositely charged surface, two regimes can be distinguished based on the effect of salt concentration on the adsorption. We call these the *screening-enhanced adsorption* regime and the *screening-reduced adsorption* regime. In the former regime the adsorption increases with increasing salt concentration because the repulsion between the segments is screened and a nonelectrostatic interaction between polyelectrolyte and surface is present. The adsorption decreases with increasing salt concentration in the latter regime, because the mainly electrostatic attraction between polyelectrolyte and surface is screened. A transition between these two regimes can take place if the balance between the electrostatic and nonelectrostatic interactions is changed. The electrostatic interactions are determined by the segment charge and the surface charge density. The strength of the nonelectrostatic interaction is described with a χ_s parameter, the net adsorption energy in units kT. From the model calculations it appears that the *screening-reduced adsorption* regime always occurs if the interaction between polyelectrolyte and surface is only electrostatic (χ_s=0). The polyelectrolyte can then be completely displaced from the surface with salt ions. If there is a nonelectrostatic attraction between polyelectrolyte and surface (χ_s>0) the *screening-enhanced adsorption* regime shows up in most cases. Only for very low segment

charges and not too low surface charge densities, which is often the case for polyelectrolytes used in papermaking, we are dealing with the *screening-reduced adsorption* regime. The theory also predicts that the adsorbed amount shows a maximum as a function of the segment charge, irrespective of the value of χ_s. For a very low salt concentration this occurs at a segment charge of about 0.01 unit charges, or even lower.

If the counter ions have a specific interaction with the surface, the adsorption of a polyelectrolyte can pass through a maximum as a function of the salt concentration provided χ_s is not too small.

The predictions of the model calculations agree very well with experimental results reported in literature.

The careful characterization of the materials and the experimental methods we used are described in chapter 3. We showed that the microcrystalline cellulose, which we use as a model for cellulose fibers, is level-off DP cellulose. This means that we are dealing with fibers chemically cut into pieces. The microcrystalline cellulose had to be cleaned before use, because hemicellulose came off in aqueous solutions disturbing the determination of the equilibrium concentration of starch with a carbohydrate determination. This was accomplished by washing the microcrystalline cellulose with concentrated NaOH solutions. The surface charge of the microcrystalline cellulose, originating from carboxylate groups, was determined by potentiometric titrations to be about −1 C/g at pH=7, which is a little lower than reported for cellulose fibers. The specific surface area is a somewhat problematic quantity for a porous substrate as microcrystalline cellulose. Based on the adsorption of cationic polyelectrolytes with different molecular weights on microcrystalline cellulose, we estimated the accessible surface area for cationic starch to be about 6 m^2/g, which is only 10% of the surface area accessible to small ions.

We used two different types of cationic starch, namely cationic potato starch and cationic waxy maize starch. Potato starch consists of two components, an essentially linear polymer of α-1,4 glucose, called amylose, and a much larger branched polymer, called amylopectin. The fraction of amylose is about 21%. Waxy maize starch consists of amylopectin only. From their sedimentation coefficients we estimated the molecular weight of cationic amylose to be about $3.5 \cdot 10^5$ and of cationic amylopectin from potato starch between $5 \cdot 10^7$ and $5 \cdot 10^8$. The molecular weight of cationic amylopectin from waxy maize was estimated to be between $1 \cdot 10^7$ and $6.5 \cdot 10^7$. Both cationic starches showed a marked decrease in viscosity and hydrodynamic radius, as measured by dynamic

light scattering, with increasing electrolyte concentration. This indicates that cationic amylopectin has enough flexibility to shrink, even though it has a branched structure.

Special attention is paid to the methods with which the starch concentration can be determined, especially to the well-known iodine determination. It is shown that it is very important to specify the iodine and iodide concentrations in the final solution with the blue starch-iodine complex and the wavelength at which the absorbance is measured.

Finally we describe how the adsorbed amounts are measured by depletion.

In chapter 4 we investigated the adsorption of cationic amylopectin (from waxy maize, DS(Degree of Substitution)=0.035) on microcrystalline cellulose in the presence of simple electrolytes and at different pH values. The adsorption isotherms of cationic amylopectin were all of the high-affinity type, as is expected for polyelectrolyte adsorption. The plateau value of the adsorbed amount showed a maximum as a function of the salt concentration. It was also found that the adsorbed amount, in the region where it decreases with increasing salt concentration, was very sensitive to the type of cation used. We obtained a lyotropic series for the alkali cations, where the adsorbed amount in the presence of the cations decreased as $Li^+ > Na^+ \approx K^+ > Cs^+$. The trend of these experimental results could be explained very well with the theory on polyelectrolyte adsorption described in chapter 2.

The plateau value of the adsorbed amount increased with increasing pH in the same way as the surface charge. The adsorbed amount of charge was estimated to be 10% of the titratable surface charge.

Based on the dependence of the adsorption on the pH and the salt concentration, we concluded that for cationic amylopectin charge interactions are the main driving forces for adsorption on cellulose.

The adsorption of cationic potato starch (usually DS=0.035) on microcrystalline cellulose is investigated in chapter 5. Special attention is paid to the fact that cationic potato starch is a mixture of 21% amylose and 79% amylopectin. It was found that amylose adsorbs preferentially. This was attributed to a larger accessible surface area for amylose due to its ability to enter the pores of microcrystalline cellulose during the equilibration time (15 hours).

The adsorption isotherms of cationic potato starch are also of the high-affinity type. There is a strong dependence on the cellulose

concentration, caused by heterodispersity of the amylose and the amylopectin fractions.

The adsorption of cationic potato starch strongly and monotonously decreased with increasing salt concentration. It was completely displaced by salt ions at concentrations larger than 0.05 M. The divalent cations Ca^{2+} and Mg^{2+} appeared to be ten times as effective as Na^{+} in suppressing the adsorption of cationic potato starch, which is due both to their higher charge and a specific interaction with the cellulose surface. From the small difference in effect of Ca^{2+} and Mg^{2+} we concluded that the phosphate groups in cationic potato starch play no relevant role in the adsorption.

Increasing the pH led to increasing adsorption. The adsorbed amount of charge was estimated to be 10% of the titratable charge.

Finally, we investigated the effect of DS on the adsorption of cationic potato starch. At 2 mM NaCl the adsorbed amount of the starch with the lowest DS (0.017) was largest, but at 10 mM NaCl the difference between starches with DS=0.017, 0.035 and 0.047 was very small. The adsorbed amounts decreased slightly with decreasing DS. Theory on polyelectrolyte adsorption predicts that at a salt concentration of about 0.01 M the adsorbed amounts of polyelectrolytes with various segment charges can be the same indeed. The effect of segment charge is larger at lower and higher salt concentration. At a low salt concentration the starch with the lowest DS is expected to adsorb most, whereas at high salt concentration the starch with the highest DS will adsorb best.

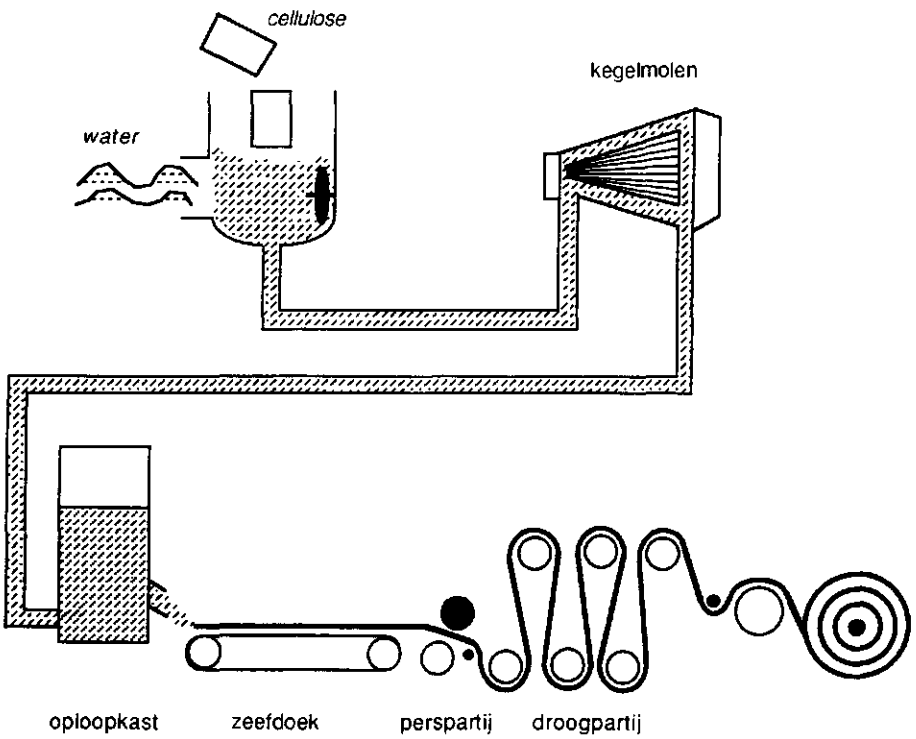
We concluded from the strong dependence on salt concentration and pH that the adsorption of cationic potato starch on cellulose is mainly driven by electrostatic attraction.

In chapter 6 we conclude that the adsorption of cationic starch on cellulose is mainly determined by the presence of charges and not by certain special properties of starch and cellulose. We point out that this thesis has general relevance because of the new light it sheds on polyelectrolyte adsorption. For papermaking this thesis is particularly relevant, because it explains the adsorption behaviour of cationic starch as that of polyelectrolytes and it therefore also improves the understanding of the adsorption of other polyelectrolytes used in papermaking. The adsorption behaviour of cationic potato starch is compared with that of cationic amylopectin from waxy maize. We suggest that this may be caused by differences in size and shape. Finally we indicate which results can be of direct relevance for papermaking in practice.

SAMENVATTING

Het onderzoek dat beschreven is in dit proefschrift heeft als achtergrond de toepassing van zetmeel bij de fabricage van papier. Alvorens in te gaan op de rol van zetmeel, zullen we eerst uitleggen hoe papier gemaakt wordt.

Papier wordt in hoofdzaak uit plantaardige cellulosevezels gemaakt, die zijn enkele millimeters lang. Meestal zijn deze vezels door een chemisch pulpproces uit hout zijn verkregen. Figuur 1 geeft een schematische weergave van het proces van papiermaken. De eerste stap is het gelijkmatig verdelen van de vezels in water; meestal zitten er dan enkele grammen vezels in één liter water. Ze worden gemalen in de kegelmolen om het oppervlak van de vezels ruwer te maken, zodat ze beter in elkaar grijpen en het papier sterker wordt. Uit de oploopkast stroomt de waterige suspensie op een bewegend zeefdoek. Hier vindt de bladvorming plaats, want de vezels grijpen in elkaar waardoor een vezelmat ontstaat. Deze vezelmat bevat nog zo'n 80% water. Dit gedeelte van de



Figuur 1. Schematische weergave van het proces van papiermaken.

papiermachine wordt de *natpartij* genoemd. Na de bladvorming wordt de vezelmat geperst en gedroogd, zodat uiteindelijk papier met een vochtgehalte van 5-8% verkregen wordt.

Naast vezels komen allerlei andere stoffen voor in papier, zoals de vulstoffen (anorganische deeltjes, bijvoorbeeld klei of calciumcarbonaat) en diverse chemicaliën, waarvan zetmeel één van de belangrijkste is. Zetmeel is de voedselreserve van planten en wordt opgeslagen in zaden, wortels en knollen (bijvoorbeeld maïs en aardappelen). Hierin zitten de zetmeelkorrels die onoplosbaar zijn in koud water. Om zetmeel te kunnen gebruiken bij het papiermaken moeten de zetmeelmoleculen opgelost worden door de korrels te koken (vergelijk het binden van een sausje met maïzena). Zetmeel wordt gebruikt om de sterkte van het (droge) papier te verbeteren en het wordt toegevoegd vóór de oploopkast. Meestal is 0.5-2% op het drooggewicht van de papiervezels hiervoor voldoende. Natuurlijk zetmeel wordt niet goed vastgehouden door de papiervezels, maar bepaalde soorten gemodificeerd zetmeel wel. Kationogeen zetmeel, dat is zetmeel waarin positief geladen groepen zijn aangebracht, werkt het beste, want de cellulose vezels hebben in water een negatieve lading. In 1957 werd het eerste patent voor kationogeen zetmeel toegekend en tegenwoordig gebruiken de meeste papierfabrieken kationogeen zetmeel. Meestal wordt kationogeen aardappelzetmeel of maïszetmeel gebruikt, in Europa vooral aardappelzetmeel en in de Verenigde Staten voornamelijk maïszetmeel.

Het is heel belangrijk dat het zetmeel goed wordt vastgehouden (papiermakers zeggen dan dat de *retentie* goed is), omdat anders niet de gewenste papiersterkte bereikt kan worden, maar ook omdat het kationogene zetmeel ervoor zorgt dat de kleine vulstofdeeltjes in het papier blijven. Als de retentie van het zetmeel slecht is en het dus door de zeef spoelt, leidt dit bovendien tot vervuiling van het proceswater en uiteindelijk tot vervuiling van het afvalwater. Vanwege allerlei milieumaatregelen moeten papierfabrieken betalen voor het lozen van afvalwater, dus ze proberen het water zo schoon mogelijk te houden. De meeste fabrieken hebben tegenwoordig hun waterkringloop gesloten om het water zo effectief mogelijk te gebruiken. Dit leidt echter tot problemen, omdat zich allerlei stoffen in dit proceswater ophopen. Eén van de belangrijkste problemen is de slechte retentie van zetmeel.

Hiermee zijn we bij het doel van het onderzoek dat beschreven is in dit proefschrift, aangeland. Hoewel er al lang zetmeel wordt gebruikt bij de fabricage van papier en ook heel veel, is het onduidelijk waarom het zetmeel wordt vastgehouden door (ook wel: adsorbeert aan) de cellulosevezels. Mede daarom is het ook niet duidelijk waardoor die

retentie verstoord wordt. In dit onderzoek is dus geprobeerd te achterhalen waarom kationogeen zetmeel adsorbeert aan cellulose vezels, en hoe dit verstoord kan worden. De methode die in dit proefschrift gebruikt is, is kolloïd-chemisch. We hebben experimenten gedaan met een zo eenvoudig mogelijk systeem, dat alleen cellulose, zetmeel en eenvoudige zouten (onder anderen keukenzout, NaCl) bevatte. Natuurlijk is dit een verregaande versimpeling van het echte papiermaken, maar dat is nodig om goed te kunnen achterhalen wat er gebeurt en waarom het gebeurt.

In hoofdstuk 2 proberen we het specifieke probleem van de adsorptie van kationogeen zetmeel aan cellulose te generaliseren door het te beschouwen als adsorptie van een polyelectrolyt[1)] aan een tegengesteld geladen oppervlak. We hebben een recente uitbreiding van de theorie voor polymeeradsorptie van Scheutjens en Fleer gebruikt om model-berekeningen te doen. Wij hebben de adsorptie van een polyelectrolyt op een tegengesteld geladen oppervlak onderzocht. Uit de model-berekeningen is gebleken dat er op grond van de invloed die de zoutconcentratie op de adsorptie heeft, twee gebieden onderscheiden kunnen worden. Wij hebben deze gebieden *afnemende adsorptie door afscherming (screening-reduced adsorption)* en *toenemende adsorptie door afscherming*[2)] *(screening-enhanced adsorption)* genoemd.

In het eerste gebied neemt de adsorptie af met toenemende zoutconcentratie, omdat de zoutionen de, hoofdzakelijk, electrostatische aantrekking tussen het polyelectrolyt en het oppervlak afschermen. In het tweede regime neemt de adsorptie toe als de zoutconcentratie toeneemt. De reden is dat de zoutionen de afstoting tussen de (gelijk geladen) polyelectrolytsegmenten afschermen, zodat het polyelectrolyt zich meer kan opkrullen en er dus meer moleculen op het oppervlak passen. Daarnaast moet er een niet-electrostatische aantrekking tussen het polyelectrolyt en het oppervlak bestaan, anders zou er bij hoge zoutconcentratie geen sprake meer zijn van adsorptie. Er kan een overgang plaatsvinden van het ene regime naar het andere als de balans tussen de electrostatische en niet-electrostatische interactie wordt veranderd. De electrostatische interacties worden bepaald door de zoutconcentratie, de lading op het polyelectrolyt (segmentlading) en de

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1)polyelectrolyt: een electrisch geladen ketenmolecuul ("polymeer").

2)afscherming: negatief geladen deeltjes in een waterige oplossing worden op grote afstand door elkaars lading afgestoten, maar als er veel zout in de oplossing zit, gaan de positieve zoutionen, die aangetrokken worden, heel dicht bij zulke deeltjes zitten, zodat ze de lading van die deeltjes afschermen. In zo'n geval "voelen" de geladen deeltjes elkaar veel minder.

lading op het oppervlak (wandladingsdichtheid). De intensiteit van de niet-electrostatische interactie wordt beschreven met een variabele die aangeduid wordt met χ_S. Dit is de netto adsorptie-energie (in eenheden kT[3]).

Uit de modelberekeningen blijkt dat de adsorptie altijd *afneemt* door afscherming als de interactie tussen polyelectrolyt en oppervlak alleen electrostatisch van aard is (χ_S=0). Het polyelectrotyt kan dan volledig van het oppervlak verdrongen worden door zoutionen. Als er een niet-electrostatische interactie met het oppervlak is (χ_S>0), neemt vrijwel altijd de adsorptie *toe* met toenemende zoutconcentratie. Alleen als de segmentlading erg laag is en de wandladingsdichtheid niet te klein, hetgeen vaak het geval is voor polyelectrolyten die in de fabricage van papier gebruikt worden, hebben we te maken met *afnemende adsorptie door afscherming*. De theorie voorspelt ook dat de geadsorbeerde hoeveelheid door een maximum gaat als functie van de segmentlading onafhankelijk van de waarde van χ_S. Voor lage zoutconcentratie verschijnt dit maximum bij een segmentlading van 0.01 eenheidladingen, of bij een nog lagere segmentlading.

Als de tegenionen een specifieke (niet-electrostatische) wisselwerking hebben met het oppervlak, kan de adsorptie van een polyelectrolyt als functie van de zoutconcentratie door een maximum gaan, mits χ_s niet te klein is.

De voorspellingen van de modelberekeningen komen goed overeen met de experimentele resultaten uit de literatuur.

De zorgvuldige karakterisering van de materialen die wij gebruikt hebben staat beschreven in hoofdstuk 3, evenals de gebruikte methoden. Wij laten zien dat microkristallijn cellulose, dat wij gebruikt hebben als model voor cellulose vezels, "level-off DP" cellulose is. Dat betekent dat we te maken hebben met vezels die chemisch in stukjes geknipt zijn. Voor gebruik moest de microkristallijne cellulose schoongemaakt worden, omdat er in waterige oplossing hemicellulose vrijkwam dat de bepaling van de evenwichtsconcentratie van zetmeel met een koolhydraatbepaling verstoorde. De microkristallijne cellulose werd daarom met geconcentreerde loog (NaOH) oplossingen gewassen. De wandlading van microkristallijne cellulose, afkomstig van dissociërende carboxylzuurgroepen, werd bepaald met potentiometrische titraties. De wandlading neemt toe met toenemende pH. Wij vonden een lading van

[3] kT: dat is de energie die één molecuul heeft ten gevolge van de warmte van zijn omgeving. Bij kamertemperatuur is dat ongeveer $4 \cdot 10^{-21}$ Joule.

-1 C/g bij pH[4]=7, hetgeen wat lager is dan de lading voor cellulose vezels. Het specifiek oppervlak is een problematische grootheid voor een poreus oppervlak zoals microkristallijne cellulose. Met behulp van de adsorptie van kationogene polyelectrolyten met verschillende molecuulgewichten, schatten wij dat het beschikbare oppervlak voor kationogeen zetmeel ongeveer 6 m^2/g is, hetgeen 10% is van het oppervlak beschikbaar voor kleine ionen.

Wij hebben twee verschillende soorten kationogeen zetmeel gebruikt, te weten kationogeen aardappelzetmeel en kationogeen zetmeel uit wasmaïs (een variëteit van maïs). Aardappelzetmeel bevat twee componenten, een voornamelijk lineair polymeer van α-1,4 glucose, dat amylose genoemd wordt, en een veel groter vertakt polymeer, dat amylopectine heet. Ongeveer 21% van het totaal is amylose. Zetmeel uit wasmaïs bevat alleen amylopectine. Met behulp van de sedimentatiecoëffiënten schatten we het molecuulgewicht van amylose op $3.5 \cdot 10^5$ en dat van amylopectine uit aardappelzetmeel tussen $5 \cdot 10^7$ en $5 \cdot 10^8$. Het molecuulgewicht van amylopectine uit wasmaïs ligt tussen $1 \cdot 10^7$ en $6.5 \cdot 10^7$. Zowel de viscositeit als de hydrodynamische straal, gemeten met dynamische lichtverstrooiing, van beide kationogene zetmelen namen sterk af met toenemende zoutconcentratie. Dit geeft aan dat kationogeen amylopectine flexibel genoeg is om te krimpen, ook al is het vertakt.

We besteden speciale aandacht aan de methodes waarmee de zetmeelconcentratie bepaald kan worden, in het bijzonder aan de bekende jodiumbepaling. Het blijkt dat het erg belangrijk is zowel de jodium en de jodide concentratie in de blauwe zetmeel-jodium oplossing te specificeren als de golflengte waarbij de extinctie van het complex gemeten wordt.

Tenslotte beschrijven we hoe de geadsorbeerde hoeveelheden met behulp van depletiemetingen[5] worden bepaald.

In hoofdstuk 4 onderzoeken we de adsorptie van kationogeen amylopectine (uit wasmaïs, DS[6]=0.035) aan microkristallijne cellulose, in de aanwezigheid van eenvoudige zouten en bij verschillende pH's. De

[4]pH: zuurgraad. Hoe lager dit getal, hoe zuurder de oplossing. Als pH=7, is de oplossing neutraal. Kraanwater heeft een pH van ongeveer 7.

[5]depletiemeting: aan een oplossing met een bekende concentratie zetmeel wordt een bepaalde hoeveelheid cellulosepoeder toegevoegd. Na een nacht schudden wordt de oplossing van het het poeder gescheiden en wordt de zetmeelconcentratie in de oplossing bepaald. De hoeveelheid zetmeel die uit de oplossing is verdwenen, is *geadsorbeerd*.

[6]DS=degree of substitution, ofwel: de fractie glucose-eenheden (bouwstenen van de zetmeelmoleculen) die een positief geladen groep bevat . DS=0.035 betekent dus dat er gemiddeld 3.5 geladen groepen voorkomen per 100 glucose-eenheden.

adsorptie-isothermen van kationogeen amylopectine waren allemaal van het high-affinity type, zoals te verwachten is voor polyelectrolytadsorptie. De plateauwaarde van de geadsorbeerde hoeveelheid als functie van de zoutconcentratie vertoont een maximum. De geadsorbeerde hoeveelheid, in het gebied waar deze daalt met toenemende zoutconcentratie, blijkt erg gevoelig te zijn voor het type zout dat gebruikt wordt. We vinden een lyotrope reeks voor de alkali kationen. De geadsorbeerde hoeveelheid in aanwezigheid van deze kationen neemt als volgt af: $Li^+ > Na^+ \approx K^+ > Cs^+$. Het verloop van de experimentele resultaten kan goed verklaard worden met de theorie over polyelectrolytadsorptie beschreven in hoofdstuk 2.

De plateauwaarde neemt op dezelfde manier toe met toenemende pH als de wandlading. De geadsorbeerde hoeveelheid lading wordt geschat op 10% van de titratielading.

Wij concluderen op basis van de invloed van de pH en de zoutconcentratie, dat voor kationogeen amylopectine de ladings-interacties de belangrijkste drijvende krachten voor adsorptie zijn.

De adsorptie van kationogeen aardappelzetmeel (meestal DS=0.,035) aan microkristallijne cellulose is onderzocht in hoofdstuk 5. Er wordt in het bijzonder rekening mee gehouden dat kationogeen aardappelzetmeel een mengsel van 21% amylose en 79% amylopectine is. Vanuit het zetmeelmengsel blijkt amylose preferent te adsorberen. Dit wordt toegeschreven aan een groter beschikbaar oppervlak voor amylose, omdat amylose in staat is in de poriën van microkristallijne cellulose te kruipen tijdens de evenwichtstijd (15 uur).

De adsorptie-isothermen van kationogeen aardappelzetmeel zijn ook van het high-affinity type. Er blijkt een sterke afhankelijkheid van de celluloseconcentratie te zijn, die veroorzaakt wordt door heterodispersiteit van de amylose- en de amylopectinefractie.

De adsorptie daalt sterk en monotoon met toenemende zoutconcentratie. Het kationogene aardappelzetmeel wordt zelfs helemaal verdrongen door zoutionen in zoutconcentraties groter dan 0.05 M. De tweewaardige kationen Ca^{2+} en Mg^{2+} blijken ongeveer tien keer zo effectief te zijn als Na^+ in het onderdrukken van de adsorptie van kationogeen aardappelzetmeel. Dit komt zowel door hun hogere lading als door een specifieke interactie met het celluloseoppervlak. Het kleine verschil in effect van Ca^{2+} en Mg^{2+} op de adsorptie geeft aan dat de fosfaatgroepen in kationogeen aardappelzetmeel waarschijnlijk niet van belang zijn voor de adsorptie.

Verhoging van de pH leidt tot toename in de adsorptie. Ook deze geadsorbeerde hoeveelheid lading wordt geschat op 10% van de titratielading.

Tenslotte onderzoeken we de invloed van de substitutiegraad DS op de adsorptie van kationogeen aardappelzetmeel. Bij een zoutconcentratie van 2 mM NaCl adsorbeert zetmeel met DS=0.017 het best, maar bij 10 mM NaCl is het verschil tussen zetmelen met DS=0.017, 0.035 en 0.047 erg klein. De adsorptie wordt een beetje lager als de DS lager wordt. De polelectrolyt adsorptietheorie voorspelt dat bij een zoutconcentratie van ongeveer 10 mM de geadsorbeerde hoeveelheden van polyelectrolyten met verschillende segmentlading inderdaad ongeveer hetzelfde kunnen zijn. De grootste verschillen zijn te verwachten bij lage en hoge zoutconcentratie. De geadsorbeerde hoeveelheid bij lage zoutconcentratie zal het hoogst zijn van zetmeel met de laagste DS, terwijl er bij hoge zoutconcentratie het meest van een zetmeel met de hoogste DS zal adsorberen.

De invloed van de pH en de zoutconcentratie leiden ons ook nu tot de conclusie dat de adsorptie van kationogeen aardappelzetmeel aan cellulose voornamelijk gedreven wordt door de electrostatische wisselwerking.

In hoofdstuk 6 concluderen we dat uit het onderzoek in dit proefschrift blijkt dat de adsorptie van kationogeen zetmeel aan cellulose voornamelijk bepaald wordt door de aanwezigheid van ladingen en niet door speciale eigenschappen van zetmeel en cellulose. We leggen uit dat het belang van dit proefschrift in het algemeen is dat het nieuw licht werpt op polyelectrolytadsorptie. Voor papiermaken is van bijzonder belang omdat het laat zien dat het adsorptiegedrag van kationogeen zetmeel verklaard als polyelectrolytadsorptie. Bovendien bevordert het het inzicht in de adsorptie van andere polyelectrolyten die bij papiermaken gebruikt worden. Het adsorptiegedrag van kationogeen aardappelzetmeel wordt vergeleken met dat van kationogeen amylopectine uit wasmaïs. Wij suggereren dat deze verschillen te maken hebben met verschillen in vorm en grootte van de moleculen in deze twee soorten zetmeel. Tenslotte geven we aan welke resultaten van direct belang kunnen zijn voor de praktijk van het papiermaken.

CURRICULUM VITAE

Henrica G.M. (Riet) van de Steeg was born on April 2nd 1961 in Venray, the Netherlands. She received her high school diploma (gymnasium-β) from the Boschveldcollege, Venray in 1979. In the same year she started studying Molecular Sciences at the Wageningen Agricultural University. She specialized in Physical Chemistry and she graduated (MSc) in June 1987. Her main subjects were Colloid Chemistry and Molecular Physics, and she took Biochemistry and Pedagogy & Didactics as secondary courses. She spent a training period of six months at the Medical Division of Siemens, Erlangen, Germany, working with Whole Body Nuclear Magnetic Resonance Imaging. From October 1987 to October 1991 she worked as a research assistent at the Department of Physical and Colloid Chemistry of Wageningen Agricultural University. As a post-doctoral she will stay at the Swedish Pulp and Paper Research Institute (STFI), Stockholm, from May 1992 to April 1993. After that she will start working at Hercules European Research Center, Barneveld, the Netherlands.

NAWOORD

Pas als het schrijven van het proefschrift achter de rug is, realiseer je je dat er met het afronden van het proefschrift ook een hele periode wordt afgerond. Er moet afscheid genomen worden. En zoals dat dan gaat, heb je als promovendus het voorrecht zwart op wit vast te leggen wat je er eigenlijk allemaal van vond, zónder dat het wetenschappelijk verantwoord is!

Ik kan gelukkig vanuit de grond van mijn hart schrijven dat ik het hartstikke leuk vond. Ik heb ruim vier jaar lang in alle vrijheid aan een heel uitdagend onderzoek kunnen werken in een buitengewoon stimulerende omgeving (een wereldberoemd lab, zoals sommigen zeggen). *Studenten en beginnende AIO's dienen de nu volgende zin over te slaan.* Voor de statistiek: ik heb ongeveer 90 adsorptie-isothermen gemeten. *Nu mogen ze weer doorlezen.* Door te werken aan een "toegepast" onderzoek temidden van veel "fundamenteel" onderzoek voelde ik mij in het begin wel eens wat verwijderd van de rest, maar beide typen onderzoek zijn in dit proefschrift heel aardig geïntegreerd geraakt. Ook op de vakgroep is men er inmiddels van overtuigd dat zetmeel een polymeer is.

En dan komen nu de mensen aan de beurt. Allereerst mijn drie begeleiders. Arie, ik heb veel geleerd van de onkreukbare manier waarop jij wetenschap bedrijft. Steeds ben jij in staat kritische vragen te stellen en, indien nodig, resultaten in twijfel te trekken, terwijl je tegelijkertijd je uiterste best doet om op een constructieve en enthousiaste manier gezamelijk naar oplossingen te zoeken. Martien, ik waardeer het zeer dat jij er, na ruim een jaar, als begeleider bijgekomen bent om mijn onderzoek op polymeergebied te ondersteunen. Jouw enthousiasme en kennis hebben mij zeer gestimuleerd. Bert, op de jou eigen bescheiden wijze heb jij je altijd zeer belangstellend getoond voor mijn onderzoek. Daarbij heb jij me alle ruimte en vertrouwen gegeven voor mijn eigen invulling, wat ik zeer op prijs heb gesteld.

Het is moeilijk in een paar regels recht te doen aan alle andere collega's die ervoor hebben gezorgd dat ik me heel goed thuis heb gevoeld op de vakgroep. Het in de loop van mijn tijd flink toegenomen aantal vrouwelijke collega's (een zeer goede ontwikkeling overigens) heeft daar zeer zeker aan bijgedragen. Enkele collega's wil ik in het bijzonder bedanken. Anton, door onze samenwerking in het beginstadium van mijn onderzoek heb jij mij een heleboel kneepjes geleerd waardoor ik alle latere experimenten beslist efficiënter heb uitgevoerd. Klaas, jij hebt mij zeer gestimuleerd modelberekeningen te gaan doen, altijd met belang-

stelling mijn berekeningen bekeken en ontelbare malen als zeer goede vraagbaak gefungeerd. Ik ben ervan overtuigd dat ik er dankzij jouw enthousiasme in geslaagd ben een theoretische verklaring te vinden voor het maximum van waxy maïs, hetgeen en passant ook nog een heus theoretisch hoofdstuk heeft opgeleverd. Ook de heren S en F wil ik graag bedanken voor hun bijdragen aan deze toepassing van de SF-theorie. Mijn kamergenoten Gerrit, Chris en Nynke hebben ervoor gezorgd dat kamer 115 mijn thuis op het lab was. Hoewel ik het erg jammer vond toen Gerrit mijn gezelschap verruilde voor dat van Marcel, hebben Chris en Nynke dit gat heel goed opgevuld. Chris, je was onschatbaar als vraagbaak voor de SUN en de SF-theorie. Nynke, je bent een zeer goede advokaat van de duivel als dat nodig is en, op een geheel ander vlak, heeft jouw voorbeeld me geïnspireerd tot het spelen van nog meer spelletjes Tetris. Het volgende thuis was het secretariaat, waar met iedereen een praatje te maken viel, maar natuurlijk in het bijzonder met José, wiens brede boezem altijd beschikbaar is om, indien nodig, op uit te huilen. Meestal vulden we de ruimte echter met gepraat, gelach en KNIPs. Trouwens, José, hartstikke bedankt voor het opkuisen van mijn engelse teksten!

Tenslotte wil ik de volgende mensen van buiten de vakgroep heel hartelijk bedanken voor hun bijdragen. Dr. André de la Porte, KNP, voor zijn continue belangstelling en bereidheid tot discussie, Piet Brouwer, Avebe, voor onze eerste discussies over zetmeel en papiermaken, Rob Versluijs, Kees Nederveen en Arie Hooimeijer, Vezelinstituut TNO afdeling Papier en Karton, voor de smeuiige verhalen en de levendige discussies, Jan Batelaan, AKZO, voor de snel georganiseerde cellulose-oplossing die ik wegens tijdgebrek helaas niet heb kunnen gebruiken en voor het interessante stukje conference proceedings dat je zomaar opstuurde, James Lichtenbelt, AKZO, voor de organisatie van mijn "excursie" naar Düren en de lezing in Arnhem, Cécile voor haar onbetaalbare ontdekkingstochten in de duisterste krochten van AKZO, Peter Steeneken, Nederlands Instituut voor Koolhydraat Onderzoek, de grootste zetmeelspecialist die ik tegen ben gekomen, voor de zeer nuttige discussies & artikelen en je warme belangstelling, en Daniël voor het ontplooien van ongebruikelijke activiteiten in mijn vertrouwde lab. I would also like to thank my Swedish friends Lars Ödberg and Lars Wågberg for their enthousiasm, support and very valuable discussions. Last but certainly not least, bedank ik Duncan, wiens organisatie-adviezen en morele steun zeker bijgedragen hebben aan de efficiënte afronding van mijn proefschrift.

Zij die verrekken gaat, groet u!

Riet

COLOFON

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